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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
STEPHEN LAWROSKI and ASSOCIATES, ARGONNE NATIONAL LABORATORY

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● NUMBER 3

TECHNICAL PROGRESS REVIEWS

To meet the needs of industry for concise summaries of current atomic developments, the Atomic Energy Commission is publishing this series, Technical Progress Reviews. Issued quarterly, each of the reviews digests and evaluates the latest findings in a specific area of nuclear technology and science.

The five journals published in this series are:

Isotopes and Radiation Technology, P. S. Baker, A. F. Rupp, and associates, Oak Ridge National Laboratory

Nuclear Safety, Wm. B. Cottrell, W. H. Jordan, and associates, Oak Ridge National Laboratory

Power Reactor Technology, W. H. Zinn and J. R. Dietrich, General Nuclear Engineering Corporation

Reactor Fuel Processing, Stephen Lawroski and associates, Chemical Engineering Division, Argonne National Laboratory

Reactor Materials, R. W. Dayton, E. M. Simons, and associates, Battelle Memorial Institute

Each journal may be purchased from the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., 20402. *Isotopes and Radiation Technology* at $2.00 per year for subscription or $0.55 for individual issues; the other four journals at $2.50 per year and $0.70 per issue. See back cover for remittance instructions and foreign postage requirements.

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REACTOR FUEL PROCESSING

A REVIEW OF RECENT DEVELOPMENTS

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC,
by STEPHEN LAWROSKI and ASSOCIATES,
ARGONNE NATIONAL LABORATORY

SUMMER 1964

VOLUME 7

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Foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho Divisions. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., P. Fineman, A. A. Jonke, S. Lawroski, W. J. Mecham, D. Paige, J. Royal, J. Simmons, R. K. Steunenberg, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

Fuel-Processing Plans

Commercial Development of Processing at Hanford

Commercial processing of nuclear materials is the object of recent plans to modify the scope of the work at Hanford. It is anticipated that Hanford will become the center of nuclear industry in the Northwest. This program is intended to begin a major and diversified commercial development at the Hanford area. The AEC has budgeted $9 million in fiscal year 1965 to support fabrication of fission products into useful forms.[1,2] Besides new facilities to process and encapsulate the fission products so that they may be produced and marketed on a commercial basis, an existing nuclear production reactor and certain existing chemical processing and waste-management facilities are available for commercial use. Also, an invitation has been extended by AEC for not-for-profit organizations to submit proposals for the operation of AEC-owned Hanford laboratory facilities. The new contractor for Hanford Laboratories will be enabled and expected to solicit research and development work from private organizations and government agencies. The contractor of Hanford Laboratories will also be expected to develop a cooperative relation with universities in the area. The Hanford Laboratories' original mission was primarily that of supporting production operations, and its present employment totals approximately 1800. The Laboratories' facilities represent a government investment of some $85 million, and the current operating budget is over $20 million.[3]

General Electric Company, heretofore the sole contractor of all Hanford facilities, will gradually withdraw in favor of new contractors. The plan for the commercial development of Hanford follows a previously announced schedule to shut down certain production reactors in accordance with a decision to reduce plutonium production.

An Engineering Design and Cost Study for a Hanford Isotopes Production Plant

Existing facilities at Hanford are being used to meet the current requirements for fission-product concentrates. However, full utilization of the potential that fission-product power sources offer is unlikely without the low costs attainable through large-scale, integrated production of encapsulated materials at the source of supply. This consideration fits in with plans of the Hanford Waste Management Program, which has been looking toward chemical processing of both stored and current fission-product wastes to remove the long-lived fission products as an approach to the efficient utilization of existing waste-storage facilities. A recent Hanford report develops conceptual design and cost estimates for a large-scale isotope production plant[4] which purifies the fission products removed from the Hanford wastes and fabricates them into useful heat sources.

The conceptual Hanford Isotopes Production Plant in this study consists of a circular process building 140 ft in diameter and 69 ft in height above grade and an attached single-story service building measuring 100 by 120 ft. The process building contains a circular, concrete-shielded structure 103 ft in diameter (see Fig. I-1). This structure is divided into 11 manipulator cells and eight process vaults. All the vaults are equipped with removable cover blocks and are served by a bridge crane pivoted at the center line of the circular structure. The capital cost of the plant is estimated to be $14,300,000.

The annual operating cost is estimated to be $4,016,000 for operation at the design basis of

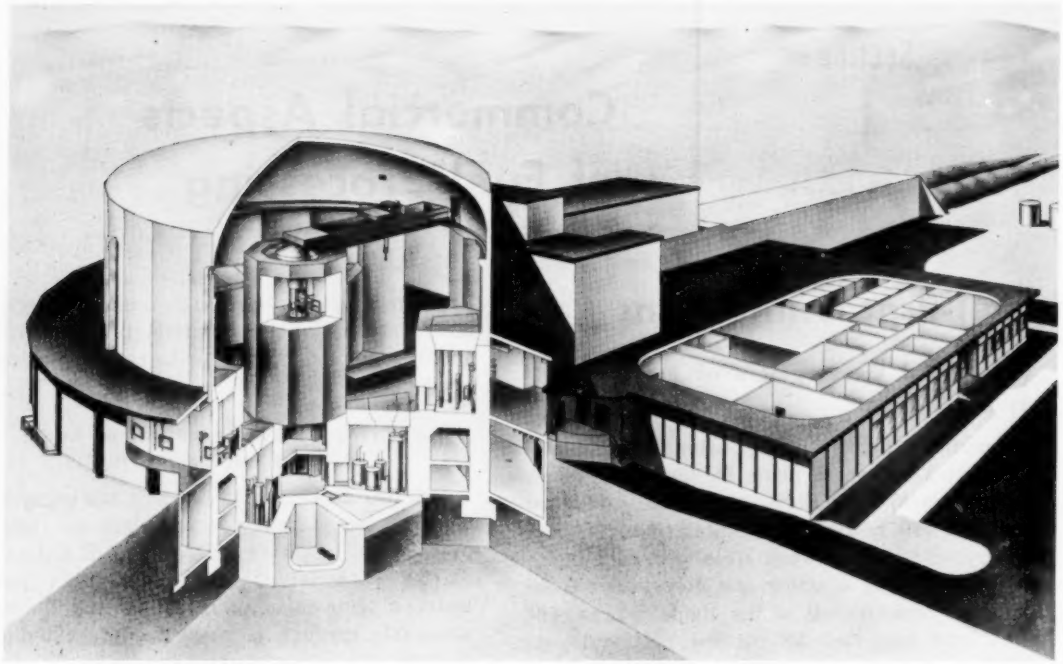

Fig. I-1 Cutaway of conceptual Hanford Isotopes Production Plant.[4]

10 megacuries of ^{90}Sr per year as the titanate, 10 megacuries of ^{137}Cs per year as borosilicate glass, 100 megacuries of ^{144}Ce per year as the oxide, and 30 megacuries of ^{147}Pm per year as the oxide, all as encapsulated heat sources; the estimated total staff is 64 people on a three-shift seven-day-week basis.

These capital and operating cost considerations result in design-basis unit costs as follows:

^{90}Sr	$0.127/curie
^{137}Cs	$0.102/curie
^{144}Ce	$0.007/curie
^{147}Pm	$0.033/curie

Details of the estimated costs are presented in the report, together with unit costs assigned to each of the four products on an apportioned basis.[4]

Isotopes Publications

Isotopes and Radiation Technology is a new journal in the AEC series of Technical Progress Reviews. The new quarterly review journal, starting with the Fall 1963 issue, gives broad coverage to all phases of radiation technology as well as isotope developments.[5] In addition, AEC began in January 1964 to issue at irregular intervals a new series of special bulletins entitled *Isotope Developments*. These bulletins are issued in the same manner as news releases and will present up-to-date technical information for users of radioisotopes.[6]

Fuel Processing in France

Among a set of articles recently published on the French civilian nuclear industry,[7] a summary was given of fuel processing in France.

The use of natural uranium for plutonium production in France led to the building and operation in 1958 of the first major nuclear fuel-processing plant at Marcoule, the center for production of plutonium for military purposes. This plant is of the Purex–tributyl phosphate (TBP) type.

A second processing plant is to be located at the Cap de la Hague site near Cherbourg and is scheduled to operate in 1966. This plant will be of a modified TBP solvent-extraction type and will have a capability for handling a wider variety of fuel elements, notably including those

made of natural-uranium–1% molybdenum alloys and irradiated in the Electricité de France (EDF) reactors.

Plans have not been made for an enriched-uranium processing plant. Since France participates with the Eurochemic program through the Organization for Economic Cooperation and Development (OECD), provision is expected to be made at the Eurochemic plant (Mol, Belgium) for treating natural and slightly enriched fuel from France.

Highly enriched uranium is employed in several swimming-pool reactors; for the processing of these fuels, consideration is being given to several European facilities. These are:

1. Modification of the Eurochemic plant to enable it to accept Materials Testing Reactor (MTR) type elements. The proposed capacity is 9 kg of ^{239}U per day.
2. Participation in the Italian EUREX project for a plant with an annual capacity of 150 to 300 kg of ^{235}U.
3. Use of the Dounreay (British) plant.

The Commissariat à l'Énergie Atomique (CEA) is also carrying out a major research program to study the nonaqueous processing of uranium fuel by halide volatility methods, i.e., processes employing uranium hexafluoride. Presumably, this program considers both high- and low-enrichment fuels.

A program for fast-breeder reactors employing the ^{238}U-^{239}Pu cycle is being formulated in France. The first reactor of this type, Rapsodie, is now being built at the Cadarache center, with participation of Euratom. The first core is to be UO_2–25% PuO_2, clad in stainless steel. Laboratory research is going on in the area of plutonium fuel processing, and plant designs are under way. A plutonium processing plant will definitely be built for new plutonium-fueled power reactors, but the location and participation have not yet been decided.

Private industry in France has always been closely associated with the CEA programs, and it is expected that industry will undertake the larger projects required as part of a developing nuclear economy.[7]

Fast-Breeder Reactor Fuel Cycle

Although thermal reactors of the oxide-fueled boiling-water type appear to be close to the point of becoming commercially competitive with conventional fossil fuels for production of electric power,[8] the fast-breeder systems require further development to achieve demonstrated feasibility of designs suitable for commercial operation. On the other hand, eventual large-scale application of fast breeders is virtually assured by its distinctive advantages for efficient long-term utilization of uranium natural resources. Private nuclear industry, now engaged in expanding commercial activities connected with thermal reactors, will increasingly be interested in the direction and timetable of developments in the AEC program for fast-breeder systems.

Frank K. Pittman, Director of Reactor Development at AEC, described the long-range (25 years) research and development program of AEC directed toward the objective of placing in operation by 1989 a commercially, economically competitive plant of the fast-breeder type having an electrical generating capability[9] of 1000 Mw. All areas of technology are to be focused on this objective.

Considerable initial progress in fast-breeder development has been embodied in the metal-fueled systems in EBR-I, the Fermi reactor, and in the integrated fuel-cycle system of the EBR-II reactor. Although metal-fuel development and demonstration will continue, the expanded fast reactor development program will feature the evaluation of ceramic fuels because of the economic promise of their high burnup potential. Although it has been determined in recent fuel-irradiation studies that high fuel burnups can be attained with mixed plutonium-uranium oxides, it was stated that final judgment regarding the relative merits of metallic or nonmetallic fuels should wait until tests have been made of metallic fuels in EBR-II and until mixed oxide fuels have been likewise evaluated by irradiation in EBR-II or the Fermi reactor. Current emphasis in the ceramic fuel development will be directed toward obtaining needed physics data.

For fast (unmoderated) reactors, sodium (rather than water) will be the coolant, its use entering into the reactor design as an element of control and safety in operation (sodium void coefficient). Accordingly, sodium technology research and development will be supported. Also, steam generators will be tested at the Sodium Components Test Installation (SCTI) near Los Angeles.

Because commercial fast-breeder economics depends largely on fuel-cycle costs, the goal of

the entire program is one of evaluation and demonstration of the fuel cycle. Conceptual design studies of 1000-Mw(e) fast reactor systems are now being prepared to guide the program. The program is coordinated on four target dates: 1967, when a decision between metal and oxide fuels may be possible; 1969, when carbide tests should be completed and when the plans provide that many decisions are to be made with regard to technology (including the final decision on fuel type); 1973, when plans call for operation of a reactor prototype; and 1989, when plans call for operation of a 1000-Mw(e) commercially competitive plant.[9]

AEC Use Charges on Fuel Being Processed

The AEC has adopted a policy of limiting the use charges that reactor operators must pay on leased reactor fuel from the time it reaches commercial processing plants. According to this policy the lessee will pay use charges only for the period between the arrival at the processing plant and the time when processing should be completed according to standard processing times. The standard processing completion times for various fuels are based on those referenced for AEC-owned processing plants. Formulas for calculating this charge period for most fuels are given in the AEC notice in the *Federal Register*.[10] For fuels not yet specified, AEC will determine the processing period on request. If the actual processing time is shorter than the time calculated by the formula, the shorter period will be used as a basis for determining the use charges.

The new policy does not operate automatically on behlaf of the reactor operator. In requesting it he must supply the AEC Materials Leasing Officer with detailed information on each processing batch. The policy will apply to adequately cooled batches delivered in processable form not later than June 30, 1970. The minimum cooling periods vary with the fuel; the shortest of the specified periods is 120 days.[10]

Benefits of this policy may accrue to both the reactor operator and the chemical plant operator. The reactor operator is protected against delays in beginning processing or in completing the processing operation. The operator of the processing plant is protected against the possibility that reactor operators would expect him to compensate them for use charges they would incur if there were any delays in handling their spent fuel.[11]

Economics of the Fuel Cycle

Nuclear Power Costs

One of the factors affecting fuel-processing costs is the amount of fuel to be processed. Small (and uncertain) plant loads have been a major obstacle to the further lowering of commercial fuel-processing costs. It is expected that, once nuclear power achieves competitive standing with fossil fuels, the commercial position of fuel processing will become more favorable. That this position is near at hand is evidenced by Jersey Central Power and Light Company's announcement that commercially competitive power will be achieved in its proposed nuclear power plant[8] at Oyster Creek, N. J.

The Jersey Central nuclear power plant will produce power at a cost below 4.5 mills/kw-hr. The Jersey Central report concludes that the proposed nuclear plant will have a distinct economic advantage over two alternatives that the utility might have chosen: a coal-fired plant of the same capacity either at Oyster Creek or a mine-mouth coal plant in Pennsylvania, feeding power into the Jersey Central System by high-voltage transmission lines. Within the first five-year period, the total power costs are estimated to go below 4 mills/kw-hr. The report presents in detail the economic analysis and also indicates the engineering and operating factors that enhanced the position of nuclear power for this installation. Although the report deals specifically with a dual-cycle system, the final decision of the utility was to order a single-cycle nuclear steam plant. The boiling-water reactor, to be supplied by General Electric, has an estimated upper level ("stretch") capacity of 640 Mw(e) net. This large size favors lower overall costs.[8,12,13]

The economic assumptions of the study with respect to fuel processing are summarized in Table I-1. In the time period of operation of the proposed nuclear plant, a transition is shown from present AEC prices for nuclear fuel to estimated future commercial prices and private ownership of fuel. The fuel processing is based

Table I-1 BASIC NUCLEAR FUEL COSTS IN JERSEY CENTRAL STUDY[12]

Fuel costs	Through 1969	1970 to 4/1/73	After 4/1/73
Yellow cake, per pound	Present AEC prices	$6	$6
Separative cost, per kilogram	Present AEC prices	$25	$25
Fuel ownership	AEC	AEC	Private
Pu (239 and 241 only), per gram	$10	$8	$8

Processing costs*	Through 1974	After 1974
Per metric ton	$23,500	$21,150
Turnaround cost, per metric ton	$7,833	$7,050
Turnaround cost, minimum	$188,000	$169,200

*Based on Nuclear Fuel Services, Inc. (NFS), contract for 3% or less enriched fuel.

on a contract with a private company, Nuclear Fuel Services, Inc. (NFS).

Fuel-processing costs were reported separately[12] for the presently ordered direct-cycle station with the 640-Mw(e) rating and are given in Table I-2. The core costs are higher for the direct-cycle reactor (shown here) than for the dual-cycle system, but the higher output per core compensates for this difference and results in lower overall costs in mills per kilowatt-hour for the direct-cycle unit. The relation of fuel-processing costs to other cost elements of the fuel cycle is shown in Table I-2. No large decrease in processing costs is shown for the time period and ground rules for this study.

The enrichment of the fuel for the proposed reactor will be less than 3%, and its cladding will be zirconium. Although the Jersey Central report did not reveal the fuel-management plan, it is supposed that multiregion cores will be used with refueling about once a year.[12]

The new, lower cost of nuclear power indicated in the Jersey Central report appears to be the result of new developments in the reactor and fuel rather than in the fuel processing. On the basis of contract price of the reactor and including extra modifications, land, interest and other charges, the total steam plant cost for an output of 640 Mw(e) is reported to be about $105 per installed electrical kilowatt. This is a lower figure than would have been anticipated a year ago.[12] Some reasons for the lower reactor cost are suggested in a report of a talk by R. C. Freeman[13] of the General Electric Company. The reactor to be supplied has a 40 kw/liter specific power rating, which may be compared with the 28 kw/liter rating for the Dresden plant of Commonwealth Edison of Chicago. [The Dresden plant is a General Electric boiling-water reactor of 210 Mw(e) and has logged over 3 million Mw-hr of commercial operation.] The reactor vessel of the larger Oyster Creek unit has an inside diameter of about 17 ft. Not until late in 1963 were vessel fabricators equipped to manufacture reactor vessels for boiling-water reactors greater than 400 Mw(e). The fuel guarantee (apparently by General Electric) for the Oyster Creek reactor is 15,000 Mwd/ton on the first core and 20,000 Mwd/ton on the second, according to Freeman.

It is likely that the decision of Jersey Central to build a nuclear power plant will encourage other utility companies to take similar action, and an improved economic situation regarding fuel processing should result.

Table I-2 FUEL-CYCLE COSTS ESTIMATED FOR THE JERSEY CENTRAL STATION[12]

[Direct-Cycle System; Unit Costs Based on 640 Mw(e)]

	Total fuel costs, thousands of dollars				Mills/kw-hr			
	Core I	Core II	Core III	Core IV	Core I	Core II	Core III	Core IV
Kw-hr × 10^6	13,009.7	17,180.8	17,525.1	17,662.9	13,009.7	17,180.8	17,525.1	17,662.9
Fabrication	$10,342.7	$ 8,669.4	$ 8,445.6	$ 8,445.6	0.795	0.504	0.482	0.478
Depletion	12,084.9	13,586.8	13,368.9	13,390.6	0.929	0.791	0.763	0.758
Shipping	457.6	457.6	457.6	457.6	0.035	0.027	0.026	0.026
Processing and losses	3,688.0	3,518.0	3,357.4	3,357.4	0.284	0.205	0.192	0.190
Plutonium credit	(3,811.2)	(4,086.2)	(4,100.8)	(4,100.8)	(0.293)	(0.238)	(0.234)	(0.232)
Use charge	1,394.0	1,568.7	307.4		0.107	0.091	0.017	
Total	$24,156.0	$23,714.3	$21,836.1	$21,550.4	1.857	1.380	1.246	1.220

Fuel-Preparation Processing of Enriched Uranium

A monograph summarizing the broad subject of enriched-uranium processing involved in fuel material preparation and fuel-element fabrication has been published by authors at the Oak Ridge Y-12 plant as a guide to those interested in the technical and economic aspects of these phases of the U. S. nuclear industry.[14] The uranium isotope separations operations are not discussed from a technical standpoint, but from the standpoint of the availability and cost of enriched uranium and its bearing on fuel-element types and their fabrication. A full range of enrichments is dealt with, but more emphasis is placed on special features of high-enrichment chemical processing steps, since the lowest enrichments may be handled by techniques that are well covered in the literature on natural uranium. Individual chapters cover process chemical operations, metallurgical and ceramic operations, nuclear and radiation safety, uranium control, plant design, and economics and management. The process chemical operations include precipitation of uranium from aqueous solution, denitration, reduction of uranium oxides to UO_2, hydrofluorination of UO_2 to UF_4, and fluorination of uranium oxides and UF_4 to UF_6. In addition, uranium recycle chemistry and production of special compounds are discussed.

The basic costs arising out of production of enriched uranium are discussed under the following major topics:

1. Cost of isotope separation work at the U. S. diffusion plants
2. Influence of the price of natural uranium
3. Inventory charges
4. Blending of different enrichments
5. Possible future role of the gas centrifuge[14]

These are the major factors in determining the costs of purchased enriched fuel and of operations of enrichment, such as would be involved in toll enrichment of privately owned fuel. Toll enrichment, as such, is not discussed in this volume. Although this monograph has many items of interest to potential commercial operation, such as specialized equipment and processes, only items of economic data on preparation of fuels (including fuel-element fabrication) will be cited here.

Certain management issues for enriched-uranium processors are cited as critical to economical fuel-cycle operation. Some of these are the following:

1. Relatively high fixed costs (i.e., costs not sensitive to day-to-day operating throughput) present the manager with low incremental costs for additional process throughput in the case where the level of production has fallen below the rated plant throughput.

2. Cost advantages tend to follow locating a chemical processing plant for fuel preparation at an existing radiochemical plant or reactor site, where that is possible. The sharing of facilities, such as the analytical laboratories and service and maintenance buildings, makes savings of the order of 20% possible for the new facility.

3. With suppliers at separate sites, scheduling operations involving recycle of scrap and coordination of supplies tend to be complex and make for high inventory charges.[14]

The following are reference cases for fuel-fabrication cost for high- and low-enrichment fuel elements:

1. A hypothetical "job-shop" for production of various low-enrichment fuel-element forms (such as unalloyed uranium, uranium-zirconium alloy pieces, and UO_2 shapes) having a capacity of about 200 metric tons of uranium per year was estimated in 1957 to have a capital cost of $8.75 million. The total unit processing cost for uranium-metal slugs (unclad) was estimated at $25 per kilogram of uranium in the fabricated product.

2. Two separate 1960 cost estimates of facilities for production of low-enrichment UO_2 fuel elements at rates of 100 tons per year gave product fabrication costs of about $50 per kilogram of uranium.

3. A hypothetical high-enrichment facility capable of producing UO_2, UO_2-ThO_2, U-Al, U-Zr, U-Mo, and UF_4-NaF fuel from UF_6 feed was estimated to require a 1961 investment of $10 million for a capacity of 10 metric tons of uranium per year. The unit fuel cost was estimated as $280 per kilogram of uranium.

Estimated Costs for Commercial Fabrication of Plutonium Fuel

A report on the feasibility and economics of commercial fabrication of plutonium fuel has been published by Savannah River.[15] The costs are developed for a conceptual design of a centralized plant for the fabrication of plutonium-

bearing oxide fuels for both thermal and fast reactors that may be operating in the near future. The use of plutonium in power reactors is evaluated, and the possibilities of commercial fabrication of plutonium fuels and the kind of fabrication facilities needed are discussed. The report considers the supplies and markets for plutonium fuels, methods of making typical fuels, the health and safety requirements of a plutonium-handling facility, and the resulting construction and operating costs.[15]

The hypothetical fuel-fabrication plant is designed for oxide fuels, since the authors consider that the most probable fuels to be fabricated commercially in the near future are likely to be mixed uranium oxide–plutonium oxide elements, in the range of 1 to 4% plutonium for thermal reactors and about 20% plutonium for fast reactors.

The forecasts of the usage of such elements up to 1975 governed the authors' selection of the size of the fabrication plant, which was built as "not the minimum cost facility that might be built immediately and aimed at a short-term operating period, but represents a centralized facility, typical of a mature industry. Its capacity would serve about six reactors, each having a power of the order of 700 to 1000 Mwe."

The hypothetical plant has equipment for the two reference types of oxide fuel, for both thermal and fast reactors. The power rating of the thermal reactor reference design is 1120 Mw(t) at 80% load factor, and the average fuel exposure is 15,000 Mwd/metric ton. The 59.73 (U + Pu) metric tons of fuel are fabricated on a 130-day manufacturing cycle. The power rating for the fast reactor is 732 Mw(t) at 80% load factor. Only the core is considered; the average fuel exposure is 80,000 Mwd/metric ton. The 7.315 metric tons of core fuel are also fabricated on a manufacturing cycle of 130 days.

The fast reactor fuel consists of a nominal $\frac{1}{4}$-in.-diameter oxide-pellet fuel element, produced from coprecipitated uranium-plutonium oxide. The thermal reactor fuel consists of a nominal $\frac{1}{2}$-in.-diameter oxide fuel element of the powder-packed type. Cladding in both cases is stainless steel (type 347), with a 15-mil wall.

A financial summary is given in Table I-3. The difference between private ownership and

Table I-3 FINANCIAL SUMMARY FOR CONCEPTUAL FABRICATION PLANT FOR UO_2-PuO_2 FUEL[15]

(Units in Dollars per Week Except As Noted)

	Case A, private ownership of Pu		Case B, government ownership of Pu	
	Fast fuel	Thermal fuel	Fast fuel	Thermal fuel
Sales, kg (Pu + U)/week	332.5	2,715.1	332.5	2,715.1
Unit price, $/kg (Pu + U)	1,992	126	309	39
Net sales	662,400	341,300	102,900	105,800
Direct operating cost	40,900	66,300	39,900	58,500
Indirect cost	12,000	11,600	12,000	11,600
Cost of plutonium				
Purchase price	535,500	218,200		
Use charge			5,900	2,400
Conversion	20,200	8,200	20,200	8,200
Total manufacturing cost	608,600	304,300	78,000	80,700
Gross income	53,800	37,000	24,900	25,100
Income taxes (federal and state at 57%)	30,600	21,100	14,200	14,300
Net profit				
Per week	23,200	15,900	10,700	10,800
Per year	1,204,000	827,000	559,000	563,000
Investment, dollars				
Permanent investment	5,000,000	5,000,000	5,000,000	5,000,000
Working capital	7,044,000	3,268,000	592,000	627,000
Total	12,044,000	8,268,000	5,592,000	5,627,000
Net return on investment, %	10	10	10	10

government ownership shows up in the purchase price of plutonium and the working capital required. The plutonium price was set at \$8/g plus \$0.25/g for conversion to PuO_2 and was adjusted for 1% losses in processing, resulting in a total value of \$8.33/g. For the government-owned case, the use charge of 4.75%/year was assessed only against the basic price plus losses (\$8.08/g). Depreciation of buildings was charged at a rate of 5%/year and that of equipment at 10%/year. Detailed cost breakdowns are presented in the report. The investment in the physical plant is given in Table I-4.

$$\frac{80{,}000 \text{ Mw(t)-days}}{1000 \text{ kg fuel}} \quad \frac{0.40 \text{ electric}}{\text{thermal}} \quad \frac{10^3 \text{ kw}}{\text{Mw}} \quad \frac{24 \text{ hr}}{\text{day}}$$

$$= 769{,}000 \frac{\text{kw(e)-hr}}{\text{kg}}$$

and, for the thermal reactor,

$$\frac{15{,}000 \text{ Mw(t)-days}}{1000 \text{ kg fuel}} \quad \frac{0.40 \text{ electric}}{\text{thermal}} \quad \frac{10^3 \text{ kw}}{\text{Mw}} \quad \frac{24 \text{ hr}}{\text{day}}$$

$$= 144{,}000 \frac{\text{kw(e)-hr}}{\text{kg}}$$

The fuel-cycle costs for the fast reactor core are thus 2.6 mills/kw-hr for privately owned fuel and 0.40 mill/kw-hr for government-owned fuel. The corresponding cases for the thermal reactor fuel are 0.88 and 0.27, respectively.

Table I-4 INVESTMENT COST ESTIMATE FOR HYPOTHETICAL FABRICATION PLANT FOR UO_2-PuO_2 FUEL[15]

Engineering design and inspection			\$ 600,000
Construction cost			4,000,000
Building		\$ 600,000	
Utilities		200,000	
Equipment		3,200,000	
Process	\$2,330,000		
Heating and ventilating	800,000		
Services	70,000		
Contingencies			400,000
Total plant investment			\$5,000,000

Land costs are not included, and it is assumed that steam and other services are available at the plant perimeter. Wastes are to be handled by a commercial contractor; an allowance of \$108 to \$416/day is made for waste disposal. The plant operates three shifts per day and five shifts per week, with a total staff of 103 to 125. Fast reactor fabrication costs are given for the core only, although the plant has the capability for fabrication of an oxide blanket.

As shown in Table I-3, the fast reactor core fuel is priced at \$1992/kg (U + Pu) and \$309 (U + Pu) for the privately owned and government-owned cases, respectively. The corresponding figures for the thermal reactor fuel are \$126/kg (U + Pu) and \$39/kg (U + Pu). The fuel costs in relation to a reference fuel cycle can be found by calculating the electric power generated for the fuel fabricated and then by expressing the fuel costs in mills per kilowatt-hour. In order to do this, the reviewer assumed a reactor plant factor of 0.40 for the conversion of thermal to net electrical energy. On the basis of the fuel exposure data, the calculations of electrical energy generated per kilogram of fuel fabricated are, for the fast reactor,

In the conceptual fabrication plant, glove boxes are used to contain all plutonium operations. Although use of special hand tools is suggested, no special remote techniques are employed. It is assumed that operator protection is achieved by local shielding and by restrictions on operator time at positions of high exposure; however, a detailed analysis is not given in this report. From a figure in the report, it appears that a glove-box area of about 540 sq ft is provided for the plutonium-containing process equipment.

By interpreting this area as the "floor space" occupied by the equipment used for preparing and fabricating the UO_2-PuO_2 mixture, the reviewer calculated the following unit costs for the facility, using the costs in Table I-4: For the complete plant,

$$\frac{\$5{,}000{,}000}{540 \text{ sq ft}} = \$930/\text{sq ft}$$

and, for the plant without processing equipment,

$$\frac{\$5{,}000{,}000 - 2{,}330{,}000}{540 \text{ sq ft}} = \$490/\text{sq ft}$$

The Fuel Cycle in Plutonium Fast Reactors

A number of papers on fuel-cycle economics were presented at the September 1963 symposium sponsored by the European Atomic Energy Society on "Fuel Cycles for Nuclear Reactors" at Baden-Baden, Germany. The papers most directly connected with fuel processing of uranium and plutonium have been reviewed in previous issues of *Reactor Fuel Processing*.[16,17] Other papers, presenting basic economic analyses of reactor fuel cycles, discuss the commercial conditions under which the fuel cycle, including fuel processing, must operate in a nuclear economy. From such considerations appear definite interactions between technical and economic criteria. Such a paper was presented by the French authors Grison, Gaussens, and LeDuc on the subject of the fuel cycle of plutonium fast-breeder reactors.[18] An economic analysis is given of capital charges on the plutonium inventory in the fast reactor fuel cycle, and plans for reactor and fuel-cycle operations are presented.

The authors cite the important role in the plutonium-breeder fuel cycle played by the high cost of the inventory of plutonium in the reactor and the processing plants of the fuel recycle loop. Dollar charges on this plutonium inventory are higher than equivalent fuel inventory charges in the uranium-plutonium thermal reactor systems. However, in a breeding system, new plutonium is generated which compensates for the capital charges on plutonium inventory. On the other hand, processing losses reduce the effective breeding of the system. An analysis is given of the plutonium balance of the complete fuel cycle, and it is concluded that, under readily attainable conditions, the net annual rate of production of plutonium in terms of kilograms of plutonium bred per kilogram of inventory per year virtually matches the annual dollar interest charges on the plutonium investment in terms of dollar charges on plutonium inventory per dollar value of plutonium inventory per year; this holds for systems having fuel-cycle losses of about 2% (or less), reactor breeding ratios of about 1.4 (or higher), and capital charges of 7% (or less) per year. Under these conditions, there are no net capital charges on plutonium, and power costs may be determined without inventory and loss charges; in other words, the plutonium is "free," and the cost of operation is independent of plutonium market price. This analysis concludes that technical performance, namely breeding, can overcome the nominal economic disadvantage of plutonium inventory in fast-breeder reactors.

Other factors of technical performance influencing inventory costs are the following:

1. Rate of processing and recycling of fuel (determined mainly by core burnup)
2. Residence time of fuel outside the reactor (determined by total time required for cooling, processing, refabricating, and shipping)

Single values of the above cost elements were assumed in this study. A more general study would treat them as variables, along with burnup and losses, considering the most favorable economic conditions.

A review is also given in this paper of the French fast-breeder program, including descriptions of processing methods and estimated costs of the fuel cycle. The Rapsodie fast breeder now being built is oxide fueled. The present plans favor processing by solvent extraction (TBP). Relative costs for components of the proposed Rapsodie fuel cycle are as follows: mechanical shearing, 5%; processing, 40%; nitrate-oxide conversion, 5%; fuel fabrication, 36%; and waste recycling, 14%. Although these figures were based on small-scale operations currently being carried out, they are consistent with large-scale estimates for future operations. (The "waste recycling" operation above apparently pertains to recovery of fissile material from scrap, etc. The report did not state explicitly whether fission-product waste disposal is included in the processing step.)

Overall power costs were estimated for the following conditions:

1. Fuel-processing and fuel-element fabrication costs of $1 per gram of plutonium and $3 per gram of plutonium
2. Fuel residence outside of the reactor, 12 months
3. Reactor burnups of 5 and 10%
4. Reactor breeding gains of 1.31 and 1.51; net theoretical breeding ratio of 5.8 to 12%/year
5. Plant factor of 80%
6. Intermittent fuel charging on cycles of 1.45 to 4.1 effective years' duration (corrected for plant factor)
7. Plutonium inventory in reactor, 2800 kg of plutonium; in entire cycle, 3500 to 4800 kg of plutonium
8. Rated power of 1000 Mw(e)

9. Plutonium losses of 2% for overall fuel cycle
10. No charges for plutonium inventory
11. Reactor capital costs of $200/installed kw(e)-hr; reactor life of 30 years
12. Power-plant operating cost of 1 mill/kw-hr

A summary of estimated fuel-processing and total power costs is shown in Table I-5. Power costs vary from 3.3 to 5.8 mills/kw-hr, and processing costs vary from 0.3 to 2.2 mills/kw-hr.

Table I-5 ESTIMATED COSTS OF PROCESSING AND TOTAL POWER COSTS FOR A 1000-Mw(e) FAST REACTOR[15]

(See Text for Reference Basis. Cost of Fuel Fabrication = Cost of Fuel Processing. Case A, Processing Cost Is $1 per Gram of Plutonium; Case B, Processing Cost Is $3 per Gram of Plutonium)

Reactor operating conditions		Cost of fuel processing, mills/kw-hr		Total power cost, mills/kw-hr	
Breeding gain	Burnup, %	Case A	Case B	Case A	Case B
1.31	5	0.85	2.2	4.15	5.5
	10	0.5	1.1	3.3	4.4
1.41	5	0.6	1.5	3.9	4.8
	10	0.3	0.85	3.6	4.15

Details of Fuel-Cycle Costs for a Plutonium Recycle System

Authors at Oak Ridge National Laboratory (ORNL) have published a report on the costs of the fuel cycle of large thermal reactors employing plutonium recycle.[19] This report is part of a continuing study of large desalinization reactors. The study included estimates of the cost for the natural-uranium cycle both with and without processing of the irradiated fuel assemblies.

The present report gives both capital and operating costs in detail for fuel-cycle processing steps applied to a Zircaloy-clad fuel element of the oxide type consisting of UO_2–0.5% PuO_2 (solid solution).

Capital cost estimates were made from equipment details and factored from equipment specifications and process-building requirements. Itemized costs of equipment and conceptual plant layouts are included.

The economic summary and comparison of the plutonium recycle system with a natural-uranium fuel cycle was reviewed previously.[20]

(A. A. Jonke and W. J. Mecham)

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Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

The emphasis in recent work on aqueous fuel separation processes continues to be on the solvent-extraction phase of the operation, and particularly on the performance and improvement of much-used processes. Treatment of ceramic fuel materials, including those containing plutonium, has received some attention.

Preparation of Fuel for Processing

The crushing of aluminum-uranium fuel plates for compaction, special measures for the dissolution of plutonium oxide, and the leaching of impregnated graphite are discussed.

Crushing of Brookhaven Graphite-Reactor Fuel Plates

During the last fuel-processing run at the Idaho Chemical Processing Plant (ICPP), it was necessary to crush 3000 Brookhaven Graphite Research Reactor (BGRR) fuel assemblies that were too bulky to transport to the continuous dissolver by the conventional manner at a reasonable rate. The program is reported in detail[1,2] by members of the ICPP Technical Staff.

The elements (Figs. II-1 and II-2) are 24 in. long by $2\frac{1}{2}$ in. in diameter and are constructed from Materials Testing Reactor (MTR) type aluminum-clad uranium-aluminum matrix. Figure II-1 also shows the experimental 10-ton hydraulic press used experimentally in a hot cell to crush several fuel elements. It was possible to reduce the cross-section dimension to $\frac{3}{4}$ in. (Fig. II-2) by using the full 10-ton force. Although it was reported that some cracking of the cladding occurred, tests of the worst elements in water showed no more leaching of fission products than from elements that were not crushed. Approximately 5 g of solids (1 mc/g) was dislodged from each element crushed. On this basis it was calculated that only a maximum of 10 to 15 curies would be released to the 1,500,000 gal of water in the storage basin from all 3000 crushed elements.

This press was installed in the basin, and all 3000 elements were crushed, transported, and dissolved with no difficulty, although at a rate somewhat below normal for the plant. Further tests were suggested to determine if the crushed elements could be stored in the basin over long periods, thus permitting the elements to be crushed as they arrived. (D. M. Paige)

Dissolution of UO_2-PuO_2 Fuel Cores

In one means for the utilization of plutonium in power reactors, plutonium as the dioxide is used to replace ^{235}U dioxide to obtain the desired nuclear reactivity in natural- or low-enrichment uranium dioxide fuels. In processing such fuels it is observed that the plutonium dioxide is much more difficult to dissolve in nitric acid than is uranium dioxide and that the addition of small quantities of fluoride to the dissolving acid may be necessary for a practical process. In recent work reported by the Hanford Laboratories operation,[3] a two-step procedure, which minimizes exposure of vessels to fluoride and nitric acid, has been studied for the dissolving of Plutonium Recycle Test Reactor (PRTR) mixed oxide fuel elements. Uranium dioxide is first dissolved in dilute nitric acid, and in the second step ammonium fluoride, with or without aluminum nitrate to minimize stainless-steel corrosion, is added to dissolve plutonium dioxide. It is reported that the following concentrations of ammonium fluoride in 15.5*M* nitric acid are adequate to

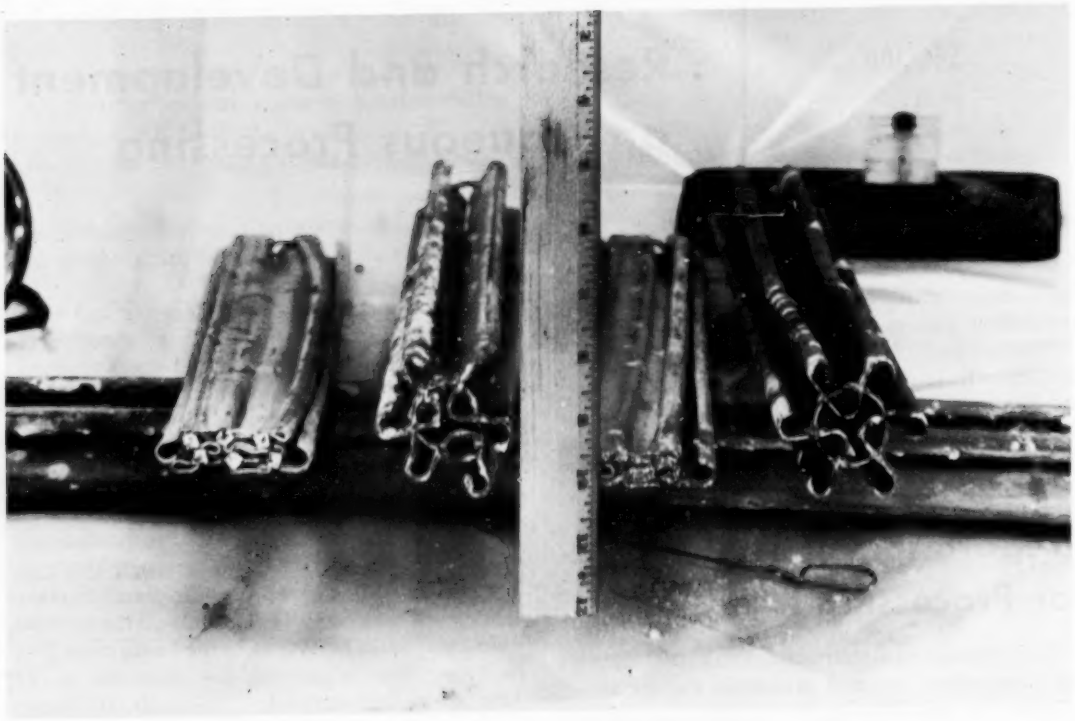

Fig. II-1 Hydraulic press and two BGRR fuel elements in multicurie cell.[1]

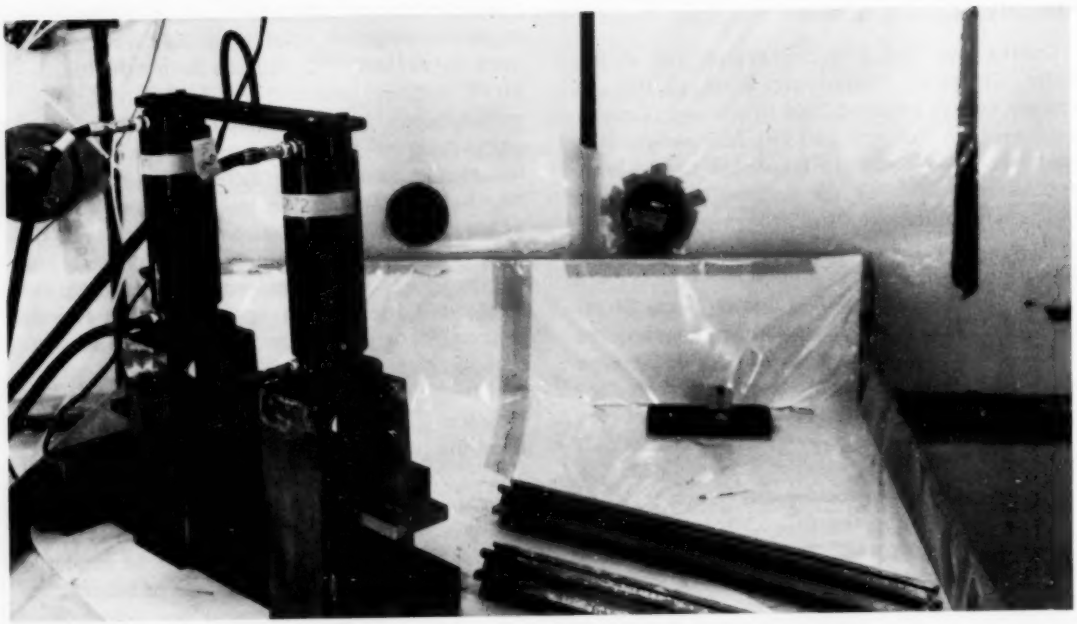

Fig. II-2 Four BGRR fuel elements, two flattened at 1500 psig and two unflattened.[1]

dissolve −325-mesh plutonium dioxide powder in the indicated times at 80°C:

Ammonium fluoride concentration, *M*	Time, hr
0.025	5–6
0.050	3.5–4.5
0.100	1–1.5

Further work[4] has indicated that the addition of aluminum nitrate is not necessary to inhibit corrosion if solution temperatures are maintained below 80°C. The two-step operation may create a criticality safety problem in large dissolving vessels, since a small concentration of plutonium dioxide, uniformly dispersed in a large amount of uranium dioxide, may be safe in a water-moderated condition, whereas the same mass of plutonium dioxide in concentrated solid form may not be safe.

Leachability of Fission Products from Impregnated Graphite

Graphite impregnated with uranyl nitrate and heated to decompose the salt to form uranium dioxide is a simple and potentially useful fuel for high-temperature power reactors. One method studied for recovery of fissionable material from such a fuel involves crushing and leaching with strong nitric acid. Consequently it is of interest to determine the leachability of fission products under similar conditions in order to assess process requirements. Iwamoto[5] has recently reported the results of some studies along this line. Both artificial graphite specimens and compressed natural graphite, irradiated at 125 and 500°C to 0.6 to 9×10^{18} neutrons/cm^2, were examined. After irradiation, crushed and ground samples were leached with a large excess of 8*N* nitric acid at the boiling point for 1 hr. Cerium, ruthenium, zirconium, and gross fission-product gamma activities were measured in the leach solutions, and the data were compared with total values obtained by digestion of samples with perchloric and nitric acid. Differences in leachability with extent of irradiation, irradiation temperature, type of graphite, or isotopes measured were relatively minor among these samples, since generally 90 to 95% of the given activity remained in the graphite. However, by heating the samples after irradiation for periods up to 19 hr at 1100 to 1400°C, residual cerium and zirconium activity could be reduced to as little as 10% by nitric acid leaching, whereas ruthenium activity was reduced to as low as 25% of the initial value.

Solvent-Extraction Separations Processes

Plant experience in the operation of a tributyl phosphate (TBP) process at the ICPP is described, and further tests of the application of tetravalent uranium for plutonium reduction are reported. Three articles that are concerned with the degradation of TBP-diluent mixtures are reviewed. These articles are from the last nine of a group of papers from the 1962 Gatlinburg Symposium on Solvent Extraction Chemistry which have recently appeared in *Nuclear Science and Engineering*. Four of the articles[6–9] have been reviewed previously.[10] A French report on work on TBP-diluent hydrolysis is also discussed.

TBP-25 Process Performance—Idaho Chemical Processing Plant

In the summer of 1963, the ICPP carried out the recovery of highly enriched uranium contained in aluminum type fuels from 12 research and test reactors over a period of several months. The duel solvent process used consisted of continuous mercury-catalyzed nitric acid dissolution, first-cycle TBP extraction, and second- and third-cycle hexone extraction. Dissolving and first-cycle extraction rates varied from 5 to 24 kg of uranium per day, and overall recovery of uranium[2] was 99.8%. A process flow sheet is given in Fig. II-3.

Detailed decontamination performance of the process was indicated by the results of analyses of four sets of samples of the products of each cycle. Individual fission-product concentrations were determined from gamma scans using a 512-channel analyzer. The feed supplied during the sampling period was largely derived from Engineering Test Reactor (ETR), MTR, and Low-Intensity Test Reactor (LITR) fuels which had similar degrees of burnup and consequently similar fission-product content. Second- and third-cycle processing was carried out after

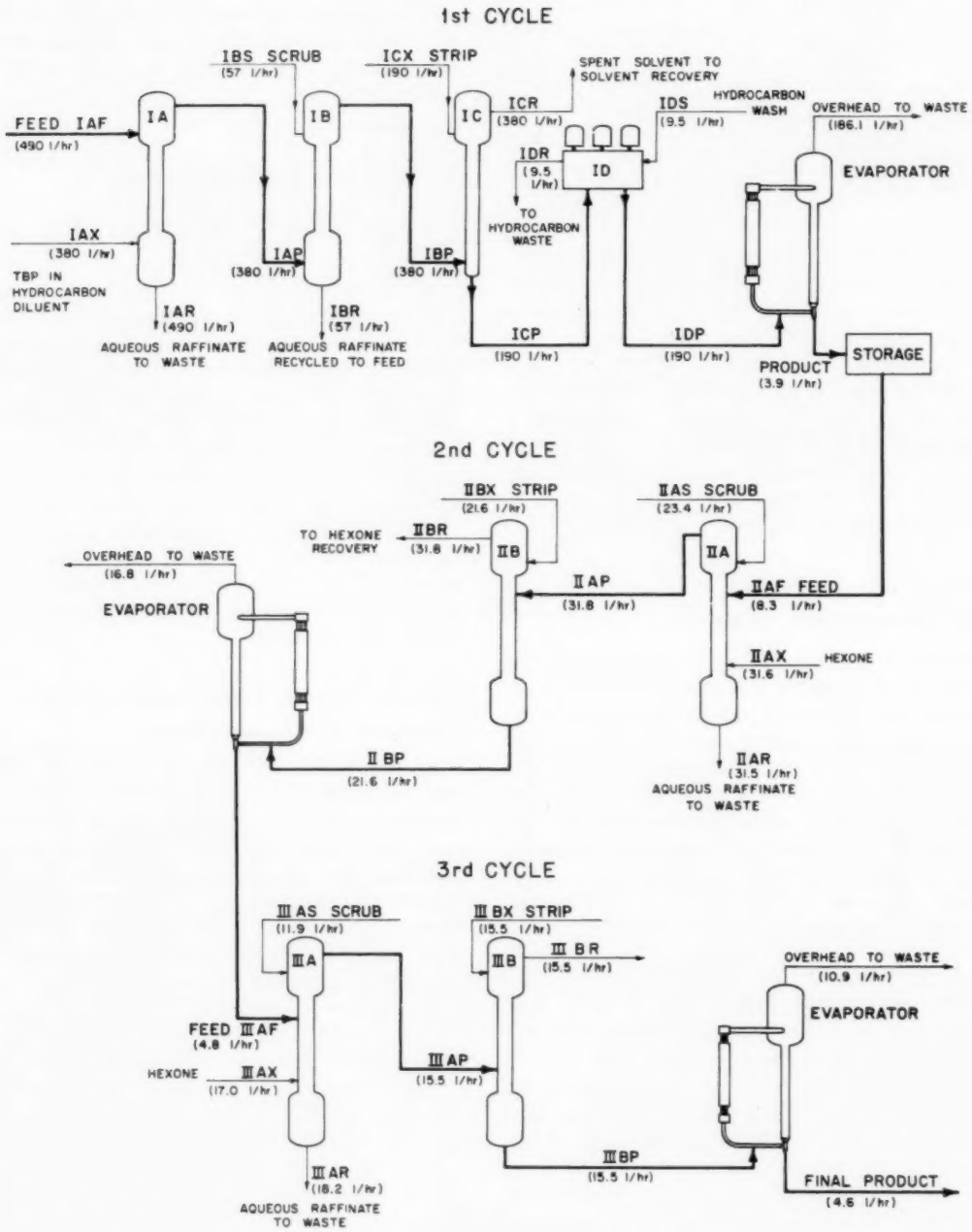

Fig. II-3 Simplified flow sheet for continuous processing of aluminum-uranium fuels at ICPP.[2]

Table II-1 SUMMARY OF LOG DECONTAMINATION FACTORS IN ICPP PROCESS STREAMS FOR RUN NO. 20 (REF. 2)

	Days from startup of cycle	Gross β	Gross γ	Ruthenium (^{103}Ru + ^{106}Ru)	Zirconium-niobium	Plutonium
1st cycle	6	3.6	2.6	3.2	1.6	0.7
	10	2.6	1.9	2.2	1.2	0.8
	13	3.1	2.4	2.8	1.9	0.4
	15	3.8	2.8	3.0	1.4	0.6
	Average	3.3	2.5	2.8	1.5	0.6
2d cycle	4	3.0	3.0	2.8	3.1	4.3
	6	2.9	3.0	2.3	3.4	4.5
	9	2.8	3.0	2.4	3.3	4.3
	12	2.9	2.8	2.5	3.2	4.4
	Average	2.9	3.0	2.5	3.3	4.4
3d cycle	4	0.4	0.2	0.9	1.7	0
	6	0.6	0.4	0.8	1.9	0.4
	9	0.6	0.3	0.8	1.6	0.1
	12	0.6	0.3	0.8	1.7	0
	Average	0.6	0.3	0.8	1.7	0
Total		6.8	5.8	6.1	6.5	5.0

completion of first-cycle extraction, with the product of the latter being mixed and stored between cycles. For this reason, variations in results obtained at different sampling times for the first and subsequent cycles cannot be correlated.

Overall log gross decontamination factors of 5.8 to 6.8 were typical of prior performance for this system.[11] The results obtained are summarized in Table II-1. It is seen that ruthenium is the limiting fission product and that, for the most part, decontamination is completed in two cycles, except that third-cycle separation of zirconium and niobium is significant (by factors of the order of 50). Plutonium rejection to waste is effected in the second cycle by addition of ferrous sulfamate to the HAS stream. No consistent trends in decontamination with processing time, as might be indicative of progressive solvent deterioration, were observed. Data previously discussed[12] on the distribution and fate of TBP degradation products [particularly dibutyl phosphate (DBP) and phosphate ion] are reviewed in detail in this report.

Tetravalent Uranium for Reduction of Plutonium in TBP Processing

To demonstrate further the utility of tetravalent uranium to reduce tetravalent plutonium to the trivalent state (and permit it to be partitioned from uranium) in TBP solvent extraction, Schlea and others[13] of Savannah River have recently reported the results of small-scale multistage mixer-settler tests of a modified Purex process. Generally, their results confirmed those of workers in the United Kingdom[14] on the advantages of substituting tetravalent uranium for ferrous sulfamate in the Purex process. At least several moles of tetravalent uranium ion were required per mole of tetravalent plutonium in order to convert the latter substantially to the trivalent state and to obtain high plutonium recoveries (0.04 to 0.2% loss). Best results were obtained by introducing the tetravalent uranium solution, stabilized with 0.2M hydrazine, separately and several stages later than the uranium-plutonium feed stream to the partitioning contactor. Adding reduced uranium directly to the feed resulted in ineffective partitioning, since the U(IV) nitrate was extracted in two or three stages. The reductant stream must also contain enough nitric acid (1.5M to 2.0M) so that the uranium is transferred to the organic phase and does not contaminate the stripped plutonium, which typically contains less than 1% uranium. Loss of plutonium is minimized by adding 0.06M to 0.2M hydrazine to the stripping solution. Comparison of partitioning in short-residence-time centrifugal extractors with that in mixer-settlers did indicate by equivalence of losses

that the rate process is controlled by mass transfer.

The reaction of hydrazine with nitrous acid in the partition contactor and the second-cycle feed adjustment vessel yields hydrazoic acid that is potentially a hazard because of the explosive nature of certain of its compounds. Since the presence of sufficient nitrous acid destroys the hydrazoic acid formed, the maximum concentration of the latter is of the order of a few hundredths molar. Although higher concentrations may be reached in distillation, the levels of hydrazine proposed were not considered to constitute a hazard. Possibilities of the precipitation of heavy-metal azides should be avoided, however.

Effect of Dibutyl Phosphoric Acid on Stripping of Uranium from TBP Diluent Mixtures

H. T. Hahn of the ICPP technical group has presented considerable work related to the effect of dibutyl phosphoric acid (HDBP) in the transfer of uranium from TBP-diluent mixtures.[15] This compound (HDBP) is a normal degradation product of TBP as a result of exposure to either radiation or chemical attack and is an undesirable constituent of TBP solvent streams in that it may cause the formation of precipitates or it may result in increased process losses.

The distribution of the compound $UO_2(DBP)_2$ at saturation between two volumes of an aqueous phase containing 0.04M to 1.05M nitric acid and one volume of a solution of TBP in a hydrocarbon diluent containing 1.0 to 30 wt.% TBP was determined. Organic-to-aqueous distribution ratios for uranium (solubility ratios) for 0.5M to 1.0M nitric acid increased from 2 to 1000 as the TBP concentration was increased from 1 to 30 wt.%, but with more dilute (0.04M) acid the solubility ratios favored the aqueous phase with a TBP concentration below 4 wt.%. This implies that, with a relatively high HDBP concentration, a significant fraction of DBP may accompany uranium during the reextraction step. The effects of HDBP concentration on uranium distribution ratios from a low-acidity aqueous phase were determined for varying initial TBP concentrations. At $10^{-5}M$ HDBP, the organic-to-aqueous distribution ratio varied from about 10^{-3} to 10^{-1} as the solvent TBP content increased from 0.09M to 0.95M. At HDBP concentrations somewhat above $10^{-3}M$, there was little effect of TBP concentration on the distribution ratio, which reached values close to 1.0 at $10^{-2}M$ HDBP. This suggested that a complex was extracted containing DBP and uranium in a 1-to-1 ratio and also containing TBP.

Solvent Deterioration in Purex Process

Orth and Olcott of Savannah River have made an interesting and detailed analysis of plant data for TBP-diluent deterioration and its effects on process performance encountered in several years' operation of the Purex decontamination and separation process recovering plutonium and uranium from irradiated reactor fuel.[16] The plant, which uses mixer-settlers in two different sizes as extraction contactors, has utilized two types of TBP diluent. At various times, periods of poor operation and abnormal fission-product behavior have been attributed to degradation of the solvent by radiolytic and chemical attack. The study was aimed at establishing how operating conditions, solvent quality, and plant performance were related and determining how various solvent recovery schemes affected solvent quality.

The analysis of plant data was based on the use of an equilibrium model for solvent condition, in which the continuously circulating solvent provides a memory for the conditions to which it was previously exposed. The concentration of a degradation product, A, at any time is the sum of that which was produced in one pass through the solvent-extraction banks and which survived one pass through the solvent washers plus that remaining from previous passes through the extraction banks which had been through the washers successively more times. A converging series is developed in which

$$A \text{ equilibrium} = \frac{R_a}{DF_a - 1}$$

where R_a is the production rate of A per pass and DF_a is the decontamination factor effected by solvent washing.

It is noted that popular scapegoats for poor plant operation, such as dibutyl phosphate (DBP), may be of small influence to long-term stability of operation compared to the effect of some material that is produced in much smaller amounts, since DBP is readily removed from solvent by alkaline washing. For some mate-

rials, very small decontamination factors are probably encountered, and a great many passes through the system are needed before equilibrium is reached.

The study is principally concerned with separate evaluation of the process decontamination performance with respect to (1) zirconium-niobium removal and (2) ruthenium removal. A mean decontamination factor for the first-cycle plutonium and uranium product streams is calculated as the reciprocal of one-half the sum of the reciprocals of the plutonium-stream decontamination factor and the uranium-stream decontamination factor.

A typical solvent performance relation is shown in Fig. II-4, where the performance attained with Adakane and Ultrasene diluents is compared on the basis of mean decontamination factor for given levels of solvent contamination with either ruthenium or zirconium-niobium. Both diluents are high-boiling kerosene type hydrocarbon mixtures. Other plant conditions were changed in the direction of maintaining better solvent quality at the time Adakane was substituted for Ultrasene; therefore improved performance cannot be ascribed unambiguously to the effect of the diluent. However, it may be seen that mean zirconium-niobium decontamination was severalfold better with Adakane than with Ultrasene for a given contamination level but that ruthenium decontamination followed a similar pattern with the two diluents. It was indicated that zirconium activity was similar in the spent solvents before washing (possibly attributable to similar DBP content) but that, in the washed solvent, zir-

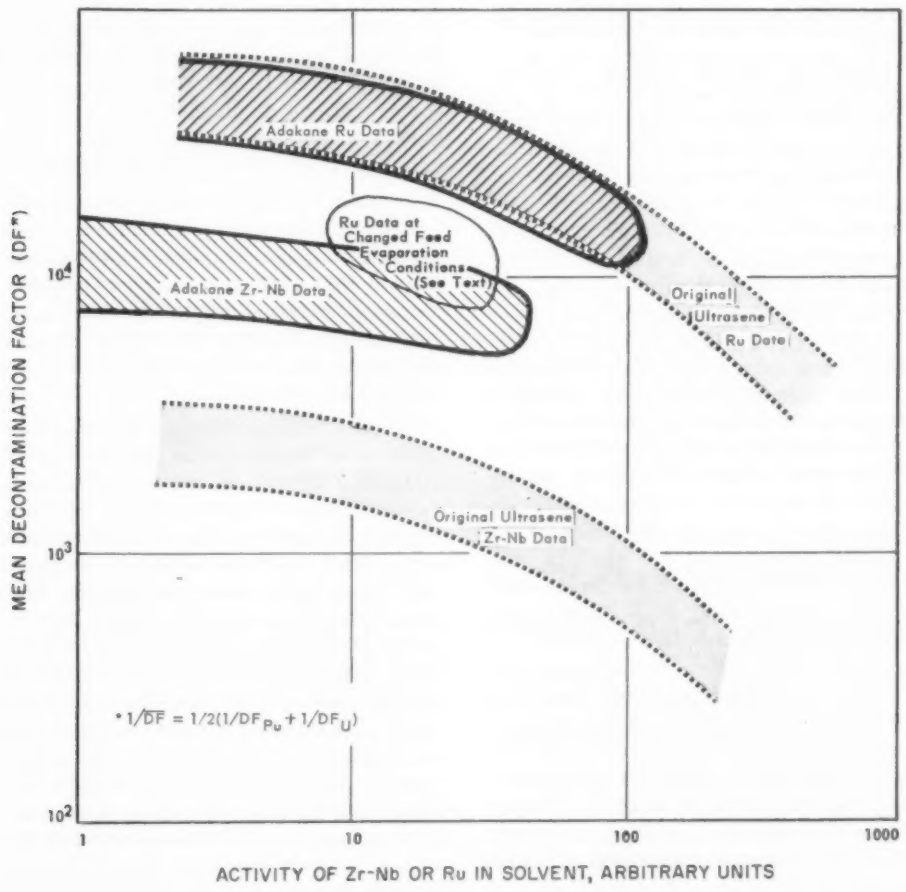

Fig. II-4 Decontamination performance with Adakane and Ultrasene diluents. Solvent contains 30% TBP.[16]

conium activity was less with Adakane than with Ultrasene, suggesting that Adakane forms less of the zirconium-containing ligands.

Various indexes of solvent quality — caustic disengaging ratio, interfacial tension with caustic, permanganate demand, Z-number,* and polarographic diffusion current — were compared. It was concluded that minor changes in any of these values are of questionable significance unless they are a part of a long-term trend. Permanganate demand generally increased with diminishing zirconium-niobium decontamination, but the value of the zirconium ligand concentration was much too small to account for the permanganate consumed. Disengaging ratios were of little significance so long as they were small (high disengaging ratios correlated well with poor ruthenium decontamination factor), and the Z-number, although it worked well for inactive solvent, was severely limited in utility for solvent with a high ruthenium background.

In the matter of solvent washing, several significant observations were made. In any given solvent, there appeared to be a core concentration of ruthenium and zirconium-niobium, which was relatively difficult to remove by typical aqueous washing reagents, and the residual ruthenium activity was more tightly bound than the zirconium-niobium activity. Undiluted alkanolamines in laboratory tests effectively removed ruthenium activity but were not tried in the plant because they appeared to be too costly. Permanganate-carbonate solution removed complexing agents both by oxidation and by absorption on manganese dioxide; carryover of MnO_2 could be a troublesome problem, however. The best order of reagents to be used involved the maximum number of alkaline-acid-alkaline cycles, and storage following an alkaline rather than acid cycle appears advantageous in minimizing hydrolysis in storage. The effects of mixing time, wash change frequency, and temperature are also reviewed.

In connection with design and planning for operation of the new United Kingdom separation plant at Windscale, which is provided for processing of natural uranium from the British Civil Power Programme, extensive experimentation was undertaken to study probable solvent degradation problems anticipated in the plant, as reported by Huggard and Warner.[17] The process uses an extraction solvent composed of 20% TBP in an odorless kerosene diluent (OK) in a Purex type flow sheet. The diluent contains about two-thirds normal and isoparaffins, one-third naphthenes, and 1% of aromatic compounds.

Batch irradiations of 20% TBP/OK, using a ^{90}Sr source or the gamma field from a fuel-element storage pond, at doses up to 125 watt-hr/liter, were found to result in high retention of both ruthenium and zirconium-niobium. *G* values* for production of nitrate and nitro compounds, carbonyl groups, and carboxylic acids ranged from about 1 to 6 under various conditions of mixing of aqueous and organic phases. Yields of various products upon irradiation are shown graphically in Fig. II-5. It will be noted that production of degradation products is generally linear with degree of irradiation, except that the degree of zirconium retention in the solvent, and presumably the content of zirconium ligands, as indicated by the Z-number, increases more rapidly as the extent of irradiation increases. Calculations showed that concentrations of zirconium ligands were very much less than concentrations of primary degradation products determined by infrared analysis.

In tests of a number of possible primary and secondary degradation products, synthesized for this purpose, only dodecylhydroxamic acid showed high ability to retain zirconium under simulated process conditions. Other hydroxamic acids were found to exhibit similar behavior and to be stable for several hours in contact with dilute nitric acid.

To determine solvent life, a recycle experiment was conducted in which TBP/OK was circulated through an extraction, backwash, and solvent process system having residence times similar to those proposed in the plant design. A 7-curie ^{90}Sr source of radiation was provided. The experiment was continued for 640 cycles under varying conditions. There was a steady increase in the retained activity level up to 480 cycles, at which time a 10-stage strip section was added with about 60% additional solvent. A gradual cleanup of the solvent then occurred and resulted in lower levels of activity. Tests indicated that solvent degradation would result in a threefold decrease in the zirconium-niobium decontamination factor for the first

*Zirconium retention index.

*Number of molecules decomposed per 100 ev of absorbed radiation.

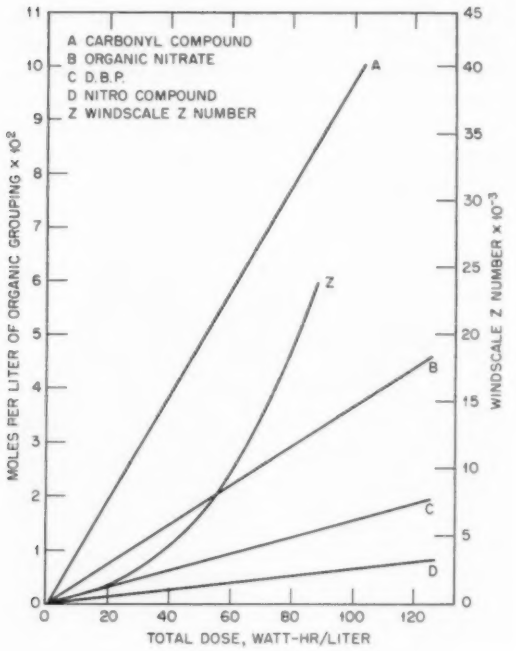

Fig. II-5 Radiation yield on degradation of 20% TBP/OK.[17]

cycle as compared with the decontamination factor obtained with fresh solvent. The results were consistent with the interpretation that zirconium ligands present in recycled, degraded solvent are little affected by passing through the whole cycle. Significant effects on ruthenium behavior were only found in solvents that had been degraded to a considerably greater extent than that resulting from 600 cycles in the recycle experiments.

Comparisons were also made of various solvent cleanup procedures, with results corresponding generally to those reported by Savannah River. Carbonate and caustic were not very effective for ligand removal, and their efficiency for activity removal fell off as solvent degradation increased. Alkaline permanganate was an effective scavenger of activity and ligands, but activity was carried over by manganese dioxide entrained by the solvent. Pure alkanolamines were found to be excellent reagents for activity and ligand removal but were thought to be too expensive to justify their use.

Isaac[18] has described studies of the Plutonium Department of the French Commissariat à l'Énergie Atomique (CEA) on the radiolysis of diluted TBP, as used in extraction of irradiated uranium at the Marcoule plant, and on the treatment of the used solvent prior to recycling to the plutonium recovery process. The solvent mixture used consisted of a 40 vol.% solution of TBP in a dodecane diluent obtained from Progil. The dodecane boiled between 160 and 220°C, had a density of 0.763 at 20°C, and consisted of both normal and branched hydrocarbons.

Radiolysis studies were carried out with a ^{60}Co source. Butyl phosphoric acids produced were determined by acidimetric titration. The values of G for the formation of monobutyl and dibutyl phosphoric acids from pure and from water-saturated TBP generally agreed with values obtained by other researchers, but somewhat unique results were obtained in the radiolysis of solvents containing nitric acid. For the formation of dibutyl phosphoric acid, the G value increased from 0.9N at 0.2N nitric acid in the solvent to 1.2N at 0.7N acid and remained at this value up to 1.1N acid. The break point corresponds to saturation with an aqueous phase 3N in nitric acid.

In studies of treatment of used solvent from the Marcoule plant, it was shown that washing with sodium carbonate solution as practiced in the plant yielded reasonably good decontamination (typically, by factors of 25 for zirconium and 5 for ruthenium). Washing with warm caustic soda produced slightly better decontamination, but other treatments studied (such as with sulfamic acid, hydrazine, mandelic acid, and oxine) resulted in little or no improvement in decontamination. Residual ruthenium in the solvent invariably limited decontamination.

(C. E. Stevenson)

Plant and Equipment Design and Operation

Nuclearly Safe Equipment Containing Boron Steel

Some of the equipment involved in the ICPP TBP-25 process runs described earlier had been redesigned to make use of boron-containing stainless-steel poison inserts so that larger vessels could be used with nuclear safety. This eliminated sole dependence on analytical and supervisory control.

This work is described in detail by Weech.[19] A product evaporator with a large poisoned disengaging head and four large-capacity poisoned storage vessels have been installed and used to advantage during the recent run. Figures II-6 and II-7 show the two vessels. The storage vessel will safely hold 840 liters with a concentration of 200 g of highly enriched uranium per liter. The evaporator head is constructed so that 200 g per liter of solution can flood the head without hazard of becoming critical (the body is already critically safe by geometry alone).

Pulse columns and mixer-settlers are also mentioned as possible vessels in which poisoned plates could be used.

Possible corrosion, selective or otherwise, could be a problem. However, tests[10] made at the ICPP indicate that, with the solutions and temperatures expected, the boron-containing stainless steel was satisfactory, although the corrosion rate in boiling 65% nitric acid was four times as high as for regular type 304 stainless steel. Specimens of the welded and nonwelded boron material have been inserted in each vessel and will be evaluated periodically.

Some cost figures given indicate that, when the value of cell space is considered, the boron-poisoned vessels have an advantage by a factor of 2 over nonpoisoned geometrically safe vessels, and, of course, in existing cells this may be the only way of increasing capacity.

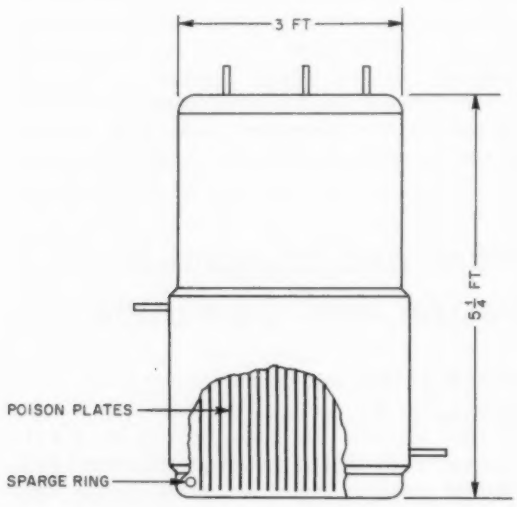

Fig. II-6 Solution-storage vessel at ICPP has vertical, evenly spaced (1.140 in.) 0.156-in.-thick poison plates of 304 stainless-steel alloy containing 1.4 wt.% boron.[19]

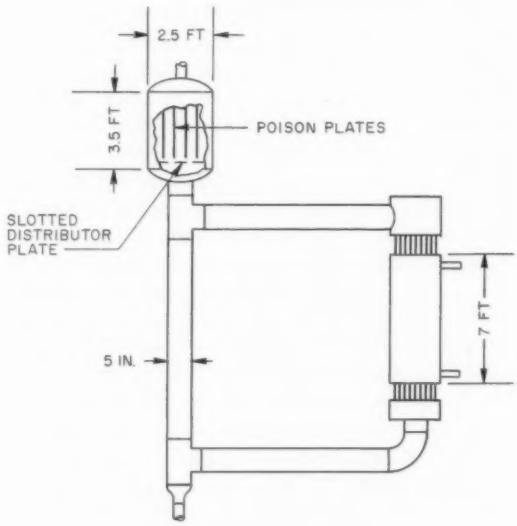

Fig. II-7 Head of evaporator at ICPP has 1.00-in.-spaced and 0.140-in.-thick poison plates of 304 stainless-steel alloy containing 1.3 wt.% boron.[19]

Centrifugal Contactor for Solvent-Extraction Processes

Since a liquid-liquid contactor is the heart of most aqueous-process systems, there is a great incentive to develop better devices. Kishbaugh of Savannah River reports[20] on such a device, which is an improved multistage centrifugal type.

A prototype unit was built and tested on cold Purex and HM (enriched uranium alloys with aluminum) process solutions with very satisfactory results. The following advantages over mixer-settlers (gravity settling) were reported:

1. Reduced exposure of solvent to radiation
2. Reduced aqueous phase and solvent inventory
3. Reduced space requirements
4. Elimination of extensive flushing between processing of different types of fuels
5. Increased nuclear safety
6. Increased versatility for wide ranges of solution densities

The unit consists of six 10-in.-diameter stages (only five were evaluated, since one

motor failed immediately). The unit shown in Fig. II-8 is complete, requiring only connectors for power, regulating air, vent, and process solutions (inlet and outlet). The essential components of a single stage are shown in Fig. II-9. They are a vertically mounted motor, which supports the centrifuge bowl, and a four-blade mixing paddle.

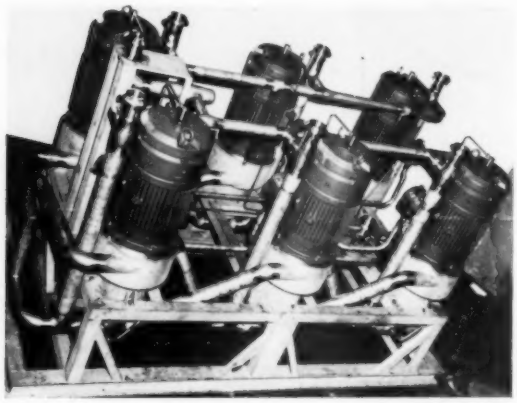

Fig. II-8 Prototype six-stage centrifugal contactor.[20]

The upper part of the bowl contains the weirs and discharge ports. The settling section, containing eight radial vanes, occupies the remainder of the bowl. Suitable baffles are provided. The rotating assembly is surrounded by a 12-in.-diameter casing that expands into a collection chamber for each phase. This casing supports the feed solution entrance arrangements. Feed solutions enter the contactor through a 3-in. tee which has a partition in the center of the vertical leg to decrease interaction of the streams. Further details on actual sizes of the various parts are reported.

Flows of organic and aqueous feeds are countercurrent between stages but are cocurrent within a stage. Solutions enter at the bottom, where they are mixed by a paddle that also pumps the dispersion into the bowl. At normal operating speed, a 300-*g* force is developed, which forces the light phase toward the center and over the light-phase weir, from which it is thrown into the light-phase collection weir and passes to the next stage. The heavy phase is forced to the bowl wall where it flows under a baffle and passes between the light-phase weir plates; it then flows under a second baffle, over a second weir, is thrown out into the heavy-phase collection chamber, and is piped to the next stage. The second baffle and weir act as a seal for the air that is introduced to control (by its pressure) the radial position of the interface.

As flow rates are increased and residence times are decreased, the width of the dispersion band inside the rotating bowl increases until entrainment occurs in one or both of the end streams. To achieve maximum capacity, the dispersion should nearly fill the space between the inner and outer edges of the annular baffle but must not extend to the exits. Since the radial position of the dispersion is a function of the air pressure on the aqueous weir, the position of the dispersion can be adjusted by either increasing or decreasing the air pressure until end streams are free of entrainment. Continued increases in flow, however, will eventually result in end stream entrainment; this flow condition is defined as the maximum hydraulic capacity of the contactor.

The report gives further detail on hydraulic capacities under varying conditions, effects of low acid concentration, mass transfer of uranyl nitrate, method of detecting motor failures, interface control methods, effects of solids in the feed, and power requirements.

High mass-transfer efficiency for uranium was attained at throughputs of 40 and 60 gal/min for Purex and HM processes, respectively. For processing undiluted tri-*n*-butyl phosphate and 3*M* nitric acid, 60 gal/min was realized. For Purex and HM process conditions, acid concentrations as low as 0.01*M* nitric acid were possible (at such a low concentration, mixer-settlers would not operate because of stable emulsions). However, with undiluted TBP and nitric acid, a stable emulsion is formed below 3*N* nitric acid aqueous concentration because of the small density difference between the phases. For Purex extraction a loss to the waste stream of only 0.0008% uranium was reported for five stages. The same five stages used for stripping left only 0.7 mg of uranium per liter at the highest process rates.

Tests showed motor failures could be detected by ammeter readings and that the unit could then be shut down (automatically), flushed easily, and removed remotely for repairs.

When manganese dioxide was used as a solid additive, at levels up to 5000 ppm, no bad effects were reported for steady-state operation. However, further work on the effect of small

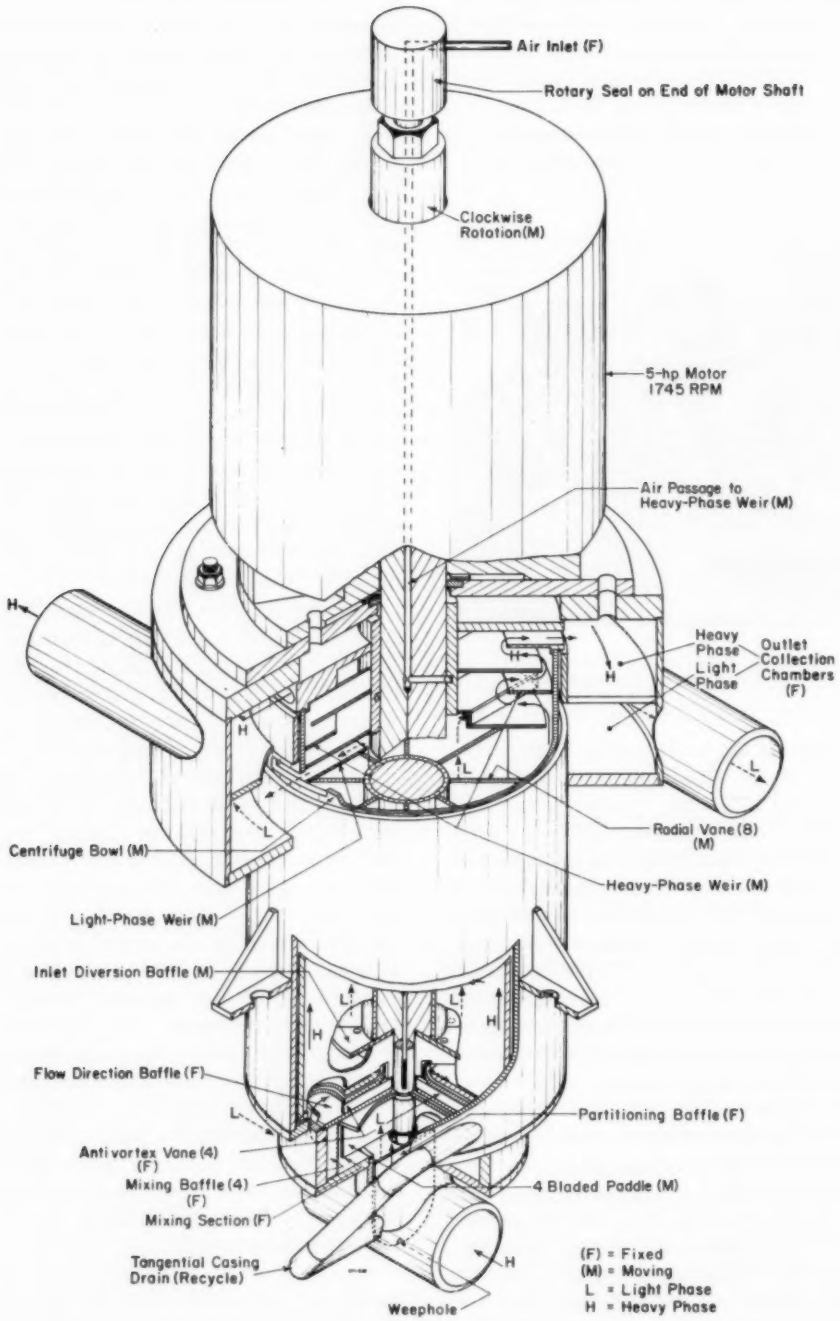

Fig. II-9 Sectional view of an individual stage of centrifugal contactor.[20] The individual stages are similar to the single-stage contactor. The essential components are shown in Fig. II-4.

amounts of solids on the operation of the centrifugal contactor will be carried out.

Power requirements essentially were linear with throughput. Kishbaugh also gives an expression for the pressure required to hold an interface. A detailed derivation of the mathematical expression for the calculation of air-weir pressure is contained in an appendix.

(D. M. Paige)

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Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

Nitroflour Process

The Nitrofluor process for treating spent reactor fuels is based on fuel dissolution or disintegration in anhydrous NO_2-HF solutions and final recovery of uranium and plutonium by volatility techniques. Several related solvents based on hydrogen fluoride and containing the reactive nitrosyl ion are being considered as alternative dissolution reagents. Recent work at Brookhaven National Laboratory (BNL)[1,2] has shown that the solvent previously designated[3,4] as NOF·3HF is actually a ternary azeotrope containing NOF, N_2O_3, and HF. Zirconium dissolves readily in this solvent at room temperature with the evolution of considerable heat, which necessitates cooling of the solvent. The heat of reaction of Zircaloy-2 in the solvent has been determined[1] at 10°C to be approximately 2900 cal per gram of Zircaloy-2. A similar value has been obtained for a solvent containing 25 mole % NO_2–75 mole % HF at 88°C, which suggests that the same reaction occurs in both solvents. The dissolution of zirconium in the ternary azeotrope results in the evolution of 4 moles of nitric oxide per mole of zirconium dissolved and the formation of a complex salt $[(NO)_2ZrF_6]$ which is only slightly soluble in the solvent and therefore precipitates from solution. Recent tests[1] have shown that aluminum dissolves in the ternary solvent with the evolution of 3 moles of nitric oxide per mole of aluminum. The complex aluminum salt formed has not been characterized, but it is probably a homolog of the zirconium salt. Aluminum dissolution rates in the ternary azeotrope at 99°C are considered satisfactory for the processing of aluminum-alloy fuels.[1]

Uranium compounds dissolve in the Nitrofluor solvents to produce nitrosylium hexafluorouranate ($NOUF_6$), which is soluble in the solvent. The uranium-bearing solution is filtered, removed from the dissolver, and evaporated to dryness. Recovery of uranium from the $NOUF_6$ residue is effected by volatility techniques. The volatilization of $NOUF_6$ in the presence of NOF gas is of considerable interest as a method for purifying uranium. Previous work[3,4] has shown that $NOUF_6$ is completely volatilized at 435°C in a NOF gas stream and that uranium tetrafluoride is collected in a downstream zone maintained at 350°C. A series of experiments has been performed[1] to define the conditions under which the $NOUF_6$ compound is volatile. It was observed that $NOUF_6$, heated in a sealed, evacuated container, deposited as $NOUF_6$ in the colder region of the vessel in the absence of NOF. Transfer of $NOUF_6$ was demonstrated in a continuously evacuated system at temperatures as low as 300°C with no appearance of UF_4 or other decomposition products in the condensed material.

Further work[2,5] has been done on defining the behavior of several fission-product elements during the volatilization of $NOUF_6$ in a stream of NOF gas. The tellurium complex, formed upon dissolution of the metal in the Nitrofluor solvent, is volatile at 160°C and condenses at 100°C. Owing to the higher volatility of the tellurium complex, it is expected that the tellurium compound would volatilize ahead of $NOUF_6$. Survey tests[2] have shown that cesium, strontium, and lanthanum do not form volatile compounds when heated in a NOF environment.

Volatility Processes for High-Enriched Fuels

Engineering-scale investigations on methods for processing graphite–uranium carbide fuels are being conducted at Oak Ridge National Laboratory (ORNL).[6] The proposed processing

scheme consists basically of oxidation of the graphite and uranium carbide by oxygen and fluorination of the oxide residue or ash by elemental fluorine, with subsequent purification of the resulting UF_6.

A series of oxidation-fluorination demonstration tests has been made[6] in a 2.5-in.-diameter nickel reactor with prototype uranium carbide–graphite fuel. For the oxidation step the reactor was heated to 700°C, and the reaction was initiated by passing pure oxygen into the reactor. The effluent gases from the reactor were passed into a separate vessel containing a sintered metal filter for removing suspended particles from the gas stream. The filter employed in the tests was sintered nickel with 35-μ openings. It was observed that an ignition temperature of at least 700°C was required for oxidation of the fuel material. Since the reaction between the fuel and oxygen is highly exothermic, the reaction vessel was cooled by an air-water mixture to provide a maximum wall temperature of 900°C. During periods of high oxidation rates, the fuel temperature was observed to rise as high as 1400°C. Tests involving 500 g of fuel required approximately 2 hr for complete oxidation. Average oxygen utilization ranged from 20 to 45%. Providing excess oxygen in the reactor made it possible to maintain the carbon monoxide concentration in the reactor off-gas below 3.5 mole %, which is less than the explosive limit of 12.5 mole % CO. The oxide residue remained entirely within the reactor and was observed to be essentially intact. The weight of solids collected on the off-gas filter was less than 0.1 g. However, in an isolated case when the oxide residue disintegrated, approximately 30 g of ash was collected on the filter.

In the fluorination step the oxide residue was contacted in place with fluorine at 400°C. The effluent gases, containing UF_6, O_2, F_2, and other volatile fluorides, passed through the sintered nickel filter at 300°C and then through a series of sodium fluoride beds, whereupon certain volatile fluorides were removed from the gas on a bed maintained at 400°C and UF_6 was recovered on a bed at 100°C. About 2 to 3 hr was required for fluorination of the ash. The average fluorine utilization was highly variable—ranging from 15 to 58% among six runs. The quantity of solid residue remaining in the reactor after fluorination was approximately 1% of the fuel charged. Little entrainment of solids from the reactor was observed during the fluorination step. The quantity of uranium sorbed on the 400°C sodium fluoride bed was considerably greater than that expected from knowledge of the NaF-UF_6 system. This uranium loss may be explained by the decomposition of UF_6 on the 400°C bed during the initial period of fluorination, when the fluorine concentration in the gas stream is low owing to high fluorine utilization. Uranium losses due to this mechanism might be prevented by introducing a separate fluorine stream downstream of the reactor. The loss of uranium, based solely on the analysis of the residue remaining in the reactor, was less than 0.1%. The quantity of unrecovered uranium was considerably greater in tests in which large amounts of NiF_2 and NiO were found in the reactor residue after fluorination.

In order to predict the effects of operating variables in large-scale processing operations, Scott[7] has prepared a mathematical analysis of the burning of graphite-uranium fuel in fixed beds. According to the analysis, the major problems to be expected in the oxidation reaction system are (1) excessive carbon monoxide content of the gas, (2) excessive fuel-rod temperature during oxidation, resulting in melting of the ash, and (3) excessive wall heat flux. The mathematical model indicated that an increase in gas flow rate results in an increase in maximum system temperature, carbon monoxide content of the off-gas, maximum wall heat flux, and length of oxidation zone up to the point that the increase in convective heat transfer results in a decrease in the system temperature, after which the maximum CO content and maximum wall heat flux decrease with increasing gas flow rate. A decrease in the oxygen content of the inlet gas (by dilution with an inert gas) results in a decrease in the maximum system temperature, CO content of the off-gas, and wall heat flux. However, decreasing the oxygen concentration by dilution results in an increase in the length of the oxidation zone. The optimum, safe oxidation time was estimated by the model to be 4 hr for the 5-in.-diameter reactor and $3\frac{1}{2}$ hr for the $2\frac{1}{2}$-in.-diameter reactor.[7]

The fuel for the High-Temperature Gas-Cooled Reactor (HTGR) is a dispersion of carbon-coated $(U\text{-}Th)C_2$ particles in a graphite matrix. At ORNL a series of laboratory-scale studies is being made to evaluate oxidation as a head-end step for processing this type fuel.[8] Pieces of simulated HTGR fuel, irradiated to approximately 10,000 Mwd/metric ton of ura-

nium plus thorium, were burned in oxygen for 5 hr to determine the fate of fission products during combustion. Two pieces of fuel were burned at 800°C and two at about 1200°C. Essentially no uranium, thorium, zirconium, or rare earths volatilized in any test. Greater than 78% of the ruthenium was volatile at 800°C, whereas approximately 97 to 99% was volatile at 1200°C. About 30% of the cesium vaporized at 800°C and 67 to 88% at 1200°C. The ThO_2-U_3O_8 combustion ash was dissolved in refluxing 13*M* HNO_3–0.04*M* HF–0.04*M* $Al(NO_3)_3$ even in those tests where the combustion was conducted at 1200°C.

Volatility Processes for Low-Enriched Fuels: Processing of UO_2 Fuels

A fluid-bed fluoride-volatility process is being developed at Argonne National Laboratory (ANL) to recover uranium and plutonium from uranium oxide fuel elements that are clad with Zircaloy or stainless steel. The proposed process involves decladding by an appropriate reaction in a fluidized bed. One scheme that is being considered for the decladding of the spent fuel employs an oxidation step to separate the uranium dioxide and plutonium dioxide from the cladding as a mixture of U_3O_8 and PuO_2. It is expected that the oxidation and subsequent fluorination steps would be performed in the same fluid-bed reactor. The oxidation of the spent oxide occurs in the lower section (oxidation zone) of the fluid bed. The U_3O_8 fines formed in the oxidation zone are transported to the upper section (fluorination zone) of the fluid-bed reactor where they are fluorinated in a fluorine gas stream introduced into the reactor at a point just above the oxidation zone. The volatile uranium and plutonium hexafluorides produced are subsequently decontaminated and separated from one another.

Jarry and associates[9] have reported the results of laboratory-scale investigations on the fluorination of U_3O_8 in a 1½-in.-diameter fluidized-bed reactor. In the tests, powdered U_3O_8 was injected into a fluid bed of alumina in the fluidizing nitrogen stream. Fluorine was introduced into the fluid bed just above the point at which the oxide powder entered the bed. A scheme employing two fluorination periods at 500°C was developed: During the first period, U_3O_8 is fed to the reactor and fluorination is carried out simultaneously with 20 vol.% fluorine in the gas phase; during the second period, pure fluorine is recirculated through the fluid bed for 5 hr. By means of this reaction scheme, more than 99% of the U_3O_8 fed to the fluid-bed reactor was converted to uranium hexafluoride.

The reaction rate of U_3O_8 with fluorine was measured[9] over the temperature range 300 to 400°C. An activation energy of 30 kcal/mole was calculated for the fluorination reaction. On the basis of these measurements, it was estimated that the time required to convert a 10-μ-diameter particle of U_3O_8 to UF_6 at 500°C was less than 2 min, which is significantly less than the average residence time of the particle in the fluid bed.

Stainless-Steel Decladding

Two alternative methods are being investigated for decladding of stainless-steel-clad UO_2 fuel elements: (1) the chemical destruction of the cladding by the high-temperature reaction with oxygen in the presence of metal fluoride promoters and (2) oxidative "decladding" by reaction of UO_2 pellets with oxygen to produce uranosic oxide, which forms as a very fine powder and readily separates from the cladding.

Jarry and associates[9] have demonstrated the oxidative removal of uranium dioxide pellets from stainless-steel cladding. Simulated fuel elements consisting of 5½-in.-long sections of ½-in.-diameter stainless-steel tubing packed with uranium dioxide pellets were oxidized in a fluid bed of alumina at 450°C with air as the oxidant and fluidizing gas. Slots (⅛ by 1/32 in.) were milled along the length of the cladding at ⅜-in. intervals to promote splitting of the cladding during oxidation. Stainless-steel tubes with a wall thickness of 30 mils were split open along their entire lengths after 4 hr of oxidation. Complete removal of U_3O_8 product was accomplished in an additional ½-hr oxidation.

Workers at BNL[1,2] have observed that stainless steel is severely attacked by reaction with oxygen at 700°C in a fluidized bed of alumina containing 1 to 7 wt.% of certain metal fluorides. A survey of metal fluoride promoters showed that the presence of FeF_3, AlF_3, CoF_2, and CoF_3 resulted in high oxidation rates (approximately 6 mils/hr). The results of small-scale rotating-bed experiments[2] indicated that a minimum concentration of 1.5 wt.% FeF_3 in the alumina bed material was required to initiate the reaction between oxygen and stainless steel at 710°C. The maximum oxidation rate was obtained with 6.9 wt.% FeF_3 at temperatures between 700 and

730°C. In tests with the FeF_3 promoter, the rate of oxidation at 710°C decreases markedly after 30 min. This decrease in reaction rate is explained by the high resistance that the oxide layer offers to the migration of oxygen to the metal surface. In tests employing AlF_3 as a promoter, it was observed that with less than 1.5 wt.% AlF_3 in the bed material no reaction occurred; maximum reaction rate was obtained in tests employing 3 to 4 wt.% AlF_3. The oxidation rate with AlF_3 showed a maximum at a bed temperature of 710°C; only a negligible rate was observed at 670°C.

Properties of Uranium Fluorides

Fluoride complexes of pentavalent uranium have been prepared by Penneman, Sturgeon, and Asprey[10] by heating UF_5 with ammonium or alkali fluorides under anhydrous conditions at temperatures up to 350°C. Uranium pentafluoride was prepared by treatment of UF_4 with gaseous UF_6 in a nickel reactor under anhydrous conditions. High-surface-area UF_4 reacted smoothly with UF_6 at 80 to 100°C to yield beta UF_5. When the temperature of the reactor was increased to 200°C, alpha UF_5 was produced. Complex fluorides with ammonium fluoride were prepared by treating intimate mixtures of UF_5 and NH_4F in Teflon bombs at temperatures of 80 to 200°C. Complex uranium-ammonium fluorides were prepared having $NH_4F : UF_5$ ratios of 1 : 1, 2 : 1, and 3 : 1. Complexes with alkali fluorides were prepared by heating together powdered mixtures of the fluorides in integral mole ratios at 300 to 350°C for several days. A series of complexes having $MF : UF_5$ ratios (M = lithium, sodium, potassium, rubidium, and cesium) of 1 : 1, 2 : 1 (except lithium and sodium), and 3 : 1 (except lithium) were characterized by X-ray powder diffraction.

Penneman and associates at Los Alamos Scientific Laboratory (LASL) have reported[11] the results of studies on the ammonium fluoride–uranium tetrafluoride–water system. It was observed that $(NH_4)_4UF_8$ is the solid phase in equilibrium at 25°C with aqueous solutions containing from 24.2 to 45.1 wt.% NH_4F. From solutions less concentrated than 24.2 wt.% NH_4F, the lower complexes $(NH_4)_2UF_6$ and $7NH_4F \cdot 6UF_4$ are obtained, but $(NH_4)_3UF_7$ is not observed. The complex $(NH_4)_2UF_6$ is polymorphic, exhibiting four crystalline modifications near room temperature. Experiments were performed which demonstrated that anion-exchange absorption of UF_4 can be accomplished on a fluoride-form resin. This demonstration clearly indicates the tendency of U(IV) to form anionic complexes with fluoride ions. Fluoride-form anion-exchange resins absorbed up to 0.60 *M* UF_4 per equivalent of exchange capacity from a water slurry of UF_4.

Sorption of Uranium Hexafluoride

Removal of technetium from uranium hexafluoride can be accomplished by selective adsorption of technetium in a bed of magnesium fluoride pellets. However, the codeposition of uranium on the magnesium fluoride to the extent of 1 wt.% has prompted the development of methods for recovering this uranium and reducing the overall uranium loss in the technetium decontamination step to less than 1 g of uranium per kilogram of sorbant.[12] It was established that physical adsorption is responsible for retention of uranium on magnesium fluoride rather than compound formation. Based on this physical property, two schemes are proposed for the recovery of the adsorbed UF_6 and its separation from technetium. Both methods result in a means for economically discarding the spent magnesium fluoride pellets. The first scheme involves preferential desorption of UF_6 by heating the MgF_2 pellets to 350°C. Technetium is poorly desorbed at this temperature. In the alternative scheme, both UF_6 and technetium are desorbed from the loaded pellet bed at 500°C in a fluorine gas stream. Uranium hexafluoride is then preferentially adsorbed on a bed of sodium fluoride pellets at 100°C. (J. Barghusen)

Fused-Salt Volatility Process Applied to Uranium-Aluminum Alloy Fuel

Volatility processes are being developed to provide an alternative to conventional aqueous processes for recovering uranium from spent nuclear fuels. The basic concept of all volatility techniques involves the conversion of uranium to a volatile compound (uranium hexafluoride) as the principal method of separating it from fission products. The progress of development at ORNL of a fused-salt volatility process applied to uranium-zirconium fuel has been reviewed in past issues of *Reactor Fuel Processing*, most recently in the Winter 1963–1964 issue. Since then, preliminary results have been reported on a study at ORNL on the adap-

tation of this process to enriched uranium-aluminum alloy fuel.[13] A significant amount of such enriched-uranium alloy fuel is discharged by existing reactors in the United States.

Because the dissolved fuel alloy comprises the fused-salt medium, the basic fused-salt processing technique has to be evaluated for the phase equilibria, the physical properties, and the dissolution and corrosion behavior of practical salt compositions containing AlF_3. Desirable characteristics of salts for use in the HF dissolution of aluminum-uranium alloys include:

1. Low cost of the salt components per unit of uranium processed
2. Liquidus temperatures below 600°C (this condition to apply both for the initial molten-salt medium and to intermediate melts containing up to at least 15 mole % AlF_3)
3. Low viscosity
4. Low vapor pressure at the operating temperature

The 600°C temperature limit is intended to provide a margin between the operating temperature and the melting point of aluminum, 660°C.

Mixtures of the component pairs $LiF-BeF_2$, $KF-LiF$, and $KF-ZrF_4$ were studied, since they form binary eutectics melting below 500°C and appear to satisfy the characteristics listed above. Tentative liquidus diagrams of the ternary systems of these pairs with AlF_3 were determined. A melt composed of 63-37 mole % $KF-ZrF_4$ is the most promising thus far; it is capable of dissolving aluminum to a concentration of 15 mole % AlF_3 (one-step flow sheet). At that concentration of AlF_3, the addition of KF to change the composition to 64.5-24.0-11.5 mole % $KF-ZrF_4-AlF_3$ makes possible the dissolution of more aluminum-uranium alloy until a final composition of 54-20-26 mole % $KF-ZrF_4-AlF_3$ is reached (two-step flow sheet). The advantage of a flow sheet based on a two-step dissolution procedure becomes evident when the unit salt costs per gram of uranium processed are compared for the two flow sheets. When a cost of $0.50 per pound for 63-37 mole % $KF-ZrF_4$ and $0.37 per pound for KF is assumed, the unit salt costs are $0.27 per gram of uranium processed for the two-step dissolution flow sheet and $0.74 per gram of uranium processed for the one-step flow sheet, with its lower capacity for dissolving aluminum. In neither dissolution step of the two flow sheets do liquidus temperatures exceed 600°C; the final salt compositions in both cases have a liquidus temperature of approximately 550°C.

Laboratory-Scale Dissolution Tests[13]

In laboratory-scale studies, dissolution of aluminum in molten $KF-ZrF_4$ with HF sparging appeared to proceed partly by hydrofluorination and partly by a metathesis type of reaction with the ZrF_4, as represented by the reactions

$$2Al + 6HF \rightarrow 2AlF_3 + 3H_2 \quad (1)$$

$$4Al + 3ZrF_4 \rightarrow 4AlF_3 + 3Zr \text{ (amorphous)} \quad (2)$$

Although the second reaction is probably correct, it has not been completely confirmed, since the amorphous product is difficult to separate and analyze in the salt matrix. Also, the amorphous material could possibly be a zirconium-aluminum alloy or ZrH_x. Continued hydrofluorination of the salt results in complete dissolution of all material, including the amorphous material.

The results of dissolution tests obtained at various molten-salt concentrations gave rates of aluminum dissolution which varied by a factor greater than 10 (see Table III-1). The use of 70-30 mole % $KF-ZrF_4$ resulted in aluminum dissolution rates of 3 to 10 mils/hr (based on micrometer measurements), the higher rates

Table III-1 ALUMINUM-DISSOLUTION-RATE TESTS IN $KF-ZrF_4$ MELT[13]

[Conditions: 0.314-In.-Diameter by 1.0-In.-Long Rods of Aluminum Suspended on Nickel Wire and Totally Submerged in 70 g of Salt in a 1-In.-Diameter Nickel Reactor; HF Flow Rate, 100 ml (STP) per Minute]

Base salt composition,* mole %		AlF_3 concentration, mole %		Dissolution rate, mils/hr	
KF	ZrF_4	Initial	Final	According to weight loss	According to micrometer measurements
70	30	5	7.2	9.4	9–10
		5	7.7	12	10–10.5
		15	15.8	6.0	6.5–7
		25	25.3	2.4	3–3.5
63	37	0	2.6	53	42
		0	6.9	25	28
		0	12.1	49	55
		0	14.7	39	42
		0	16.1	52	
		5	8.9	16	16–17
73	27	12	15.0	26	20–22

*Exclusive of AlF_3 content.

being obtained at low initial concentrations of AlF_3. In contrast, the use of 63-37 mole % $KF-ZrF_4$ always resulted in aluminum dissolution rates of approximately 20 to 50 mils/hr, depending also on the AlF_3 concentrations. It is believed that reduction of ZrF_4 at higher ZrF_4 concentrations probably accounts for the higher rates of dissolution. In one test of the two-step flow sheet (intermediate addition of KF), a satisfactory dissolution rate for aluminum (>20 mils/hr) was obtained with 73-27 mole % $KF-ZrF_4$ (see Table III-1).

Although reduction of ZrF_4 appears to be an important factor in obtaining a high dissolution rate, the concurrent reaction of aluminum with HF is necessary in order to catalyze the ZrF_4 reaction. This HF effect, therefore, enables positive control of the dissolution through control of the HF flow.

The melting point of aluminum is 660°C; therefore allowing the dissolver temperature to rise to this point is to be avoided. However, in a separate study to determine the effect of melting on the dissolution of aluminum, the onset of melting did not have serious consequences, and dissolution of the metal was achieved with continued hydrofluorination.

The most significant factor arising from the reduction of ZrF_4 by aluminum is the effect of the presence of amorphous zirconium or amorphous zirconium-aluminum alloy in the molten salt. This presence of the amorphous material leads to some thickening of the molten salt and possibly to hindering the passage of gaseous HF. Sparging with HF may result in entrainment of the reduced metal (zirconium) in the off-gas as was found in the case of the reduced nickel, molybdenum, and tin present in the zirconium-uranium alloy process. A digestion period will be necessary in aluminum-uranium alloy processing to redissolve the precipitated amorphous metal after all the original fuel alloy has dissolved.

Laboratory fluorination tests with salts representing the two flow sheets resulted in volatilization of 99.6 and 99.4% of the uranium upon fluorination at 550 to 575°C for 1.4 hr. The initial uranium concentrations were 1500 and 5300 ppm, respectively.

LABORATORY CORROSION TESTS[13]

Laboratory tests directed toward the evaluation of construction materials of the dissolver-hydrofluorinator have begun. Corrosion expected in the $KF-ZrF_4$ system for dissolving aluminum with HF has been studied for one case at Battelle Memorial Institute (BMI). In the laboratory experiment, corrosion was found to be unusually low when nickel-base alloys were exposed to 63.8-31.4-4.8 mole % $KF-ZrF_4-AlF_3$ at 600°C while dissolving type 1100 aluminum with HF. Table III-2 summarizes results of this experiment.

ENGINEERING-SCALE DISSOLUTION STUDIES[13]

On an engineering scale, sections of Low-Intensity Test Reactor (LITR) prototype elements (aluminum-clad aluminum–10 to 20 wt.% uranium) were dissolved by anhydrous HF in 62-38 mole % $KF-ZrF_4$ between 550 and 600°C

Table III-2 CORROSION OF NICKEL-BASE ALLOYS DURING EXPOSURE TO HF AND $KF-ZrF_4-AlF_3$ WITH ALUMINUM DISSOLUTION[13]

Salt: 63.8-31.4-4.8 mole % $KF-ZrF_4-AlF_3$ to 15.6 mole % AlF_3
HF rate: 10 g/hr
Temperature: 600°C (except first 5 hr, 650°C)
Run time: 200 hr
Metal dissolution: type 1100 aluminum rods, $\frac{5}{8}$ in. in diameter by $1\frac{1}{2}$ in. long

Alloy	Nominal composition, wt.%					Corrosion rate (max.), mils/month		
	Mo	Fe	Cr	Ni	Other	Liquid	Interface	Vapor
INOR-8	16	5	7	71		0.02	0.16	0.07
HyMu 80	4	16		79		0.19	0.33	0.14
79-4	4	16		79		0.41	0.77	0.31
2	10	5		85		0.06	0.21	0.08
32	2	18		80		0.08	0.31	0.30
TD Ni				98	2% ThO_2 dispersion	0.57		

in an INOR-8 vessel, 3.5 in. in inside diameter by 24 in. Two dissolutions (one partial, one complete) were made with no important difficulties. The second dissolution, in which a 2-in.-long quarter-cross-section LITR element was completely dissolved, was very smooth and rapid, as was the subsequent salt transfer. The dissolution was completed in a total of 7 hr (including a 3-hr salt cleanup period).

OUTLOOK FOR USE IN PILOT PLANT[13]

On the basis of preliminary results obtained so far, processing of alumnium-base fuels by the fluoride-volatility process appears feasible and should be amenable to techniques used in the processing of the zirconium-base fuels. Larger-scale dissolutions and fluorinations of $KF-ZrF_4-AlF_3-UF_4$ are planned in anticipation of processing full-size aluminum-base fuel elements in the Volatility Pilot Plant at ORNL. A comparison of the capacity of the present dissolver in the ORNL Volatility Pilot Plant indicates that, starting with 63-37 mole % $KF-ZrF_4$ and allowing 15 mole % AlF_3 in the product salt, one element of the Materials Testing Reactor (MTR), less end boxes, could be dissolved in about the same volume of salt as is being used to dissolve two Zircaloy-2 elements. The MTR elements are essentially the same as LITR elements. If it is assumed that the MTR elements contain 5 wt.% uranium, the product salt would contain about 2000 ppm uranium, or about the same as that in the zirconium dissolutions. In the two-step dissolution flow sheet, which calls for the intermediate addition of KF, the uranium concentration in the salt could be increased to about 4000 ppm by dissolving two elements. (W. J. Mecham)

Pyrometallurgical Processes

Pyrometallurgical processes are being developed at several atomic energy sites with the objective of reducing the costs of recycling fuels discharged from power reactors. Included in such processes are those in which metallic fuels are purified directly as metals and others in which metallic fuels and ceramic fuels are purified in liquid-metal and salt systems. The potential economic advantages of these processes lie in their ability to handle short-cooled fuels, which makes possible minimum fuel inventories, and in the avoidance or simplification of chemical conversions. Other advantages of these processes are the direct production of solid wastes, the absence of severe critical mass restrictions, and, in some processes, the retention of valuable fuel alloying additives.

EBR-II Fuel-Cycle Facility

The EBR-II Fuel-Cycle Facility is a processing plant for recovery and purification of discharged EBR-II fuel materials and for refabrication of the fuel materials for return to the reactor.[14] This reactor system will be the first to operate on a closed fuel cycle and, therefore, the first for which problems (such as buildup of heavy isotopes) inherent in continued recycle of the same fuel material can be assessed. The first core loading is an enriched-uranium alloy containing 46 wt.% ^{235}U and 5 wt.% fissium (2.5 wt.% molybdenum, 2.0 wt.% ruthenium, 0.26 wt.% rhodium, 0.19 wt.% palladium, 0.1 wt.% zirconium, and 0.01 wt.% niobium).

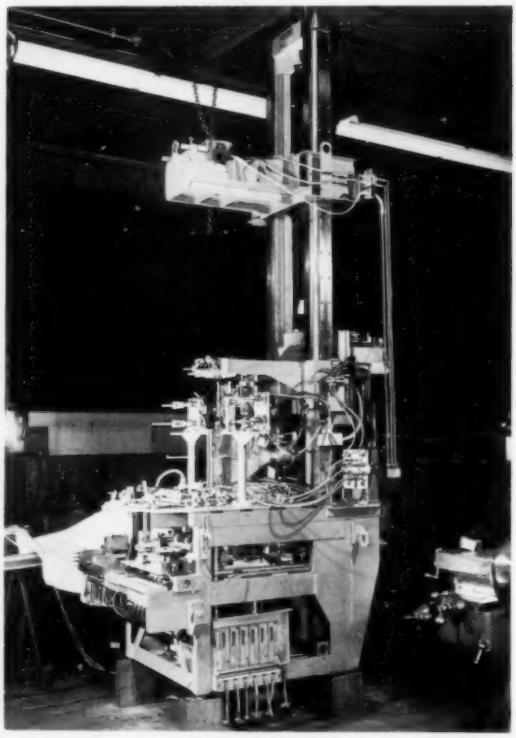

Fig. III-1 Fuel-element assembly machine.[16]

The Fuel-Cycle Facility will be used to demonstrate a number of pyrometallurgical processes, but melt refining, the most completely developed process, will be initially employed. This is a process by which most of the fission-product elements are removed from molten fuel by volatilization and by selective oxidation reactions.[14] EBR-II fuel pins (0.144 in. in diameter by 14 in. in length) will be re-formed by pressuring molten fuel into precision-bore Vycor tube molds, a process known as injection casting.

Progress continues to be made in preparing the Fuel-Cycle Facility for operation.[15,16] Recently completed equipment items that are available for installation include a fuel-element assembly machine (see Fig. III-1), the electrical programmers (Fig. III-2) that control the assembly of core and blanket fuel elements, a furnace[16] for oxidizing the residues or skull material in melt-refining crucibles, and associated equipment for dumping the oxides into storage containers. The fissionable material in the stored oxides will later be recovered by a process known as the skull reclamation process.[17] The second of two melt-refining furnaces has been installed in the Fuel-Cycle Facility and placed in operation. Shakedown testing of various equipment items is in progress.[15,16]

The skull oxidation equipment was tested[16] prior to installation in the Fuel-Cycle Facility by oxidizing the skulls remaining in six zirconia melt-refining crucibles that had previously been used for melt refining of uranium-fissium–0.65% cerium alloys. After the oxidation step the oxides were poured out, and the zirconia crucibles, which normally would be discarded to waste, were pulverized and sampled for determination of the residual uranium content. X-ray spectrochemical analyses of the six samples gave an average uranium content in the waste crucibles corresponding to only 0.18% of the original alloy charges, or 2.5% of that in the skull material. Similar values are expected when the oxidation is performed in the EBR-II Fuel-Cycle Facility.

In the EBR-II Fuel-Cycle Facility, fuel processing and refabrication operations that involve exposure of highly radioactive unclad fuel materials are conducted in a 60,000-cu ft argon-atmosphere processing cell. Schraidt and coworkers of ANL have published a report on the problems of establishing and maintaining a high-purity argon atmosphere in the processing cell.[18]

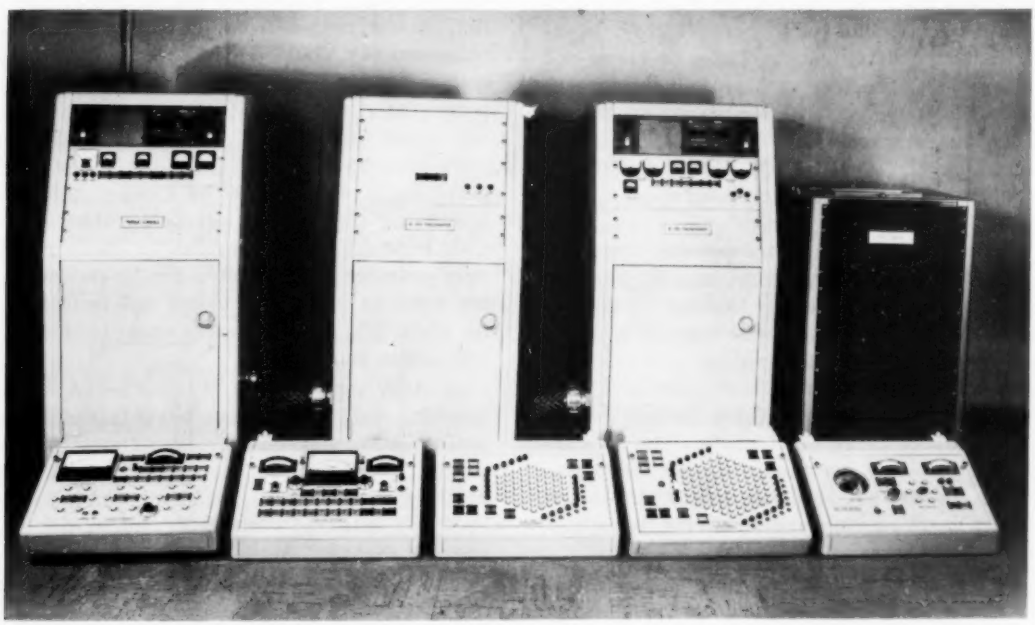

Fig. III-2 Programming and controls for assembling and testing 61-pin and 91-pin fuel elements for EBR-II.[15]

Melt-Refining Technology

In the melt-refining process to be used for the first EBR-II core, oxygen for the selective oxidation of the highly electropositive fission-product elements (the alkaline-earth and rare-earth elements) is supplied by the zirconia crucible. This process may also be used for future EBR-II metal fuels that will contain plutonium. However, an interesting alternative process is currently being investigated in which melt refining will be carried out beneath a molten halide salt layer in a beryllia crucible.[16,19] The rare-earth fission products are preferentially oxidized into the salt phase and thereby separated from uranium and plutonium. Potential advantages of this alternative process over the present EBR-II melt-refining process are higher yields and reduced operating times.

In recent studies to evaluate the use of molten salts in the melt-refining process, the chloride salts have been composed of mixtures of $BaCl_2$ and $CaCl_2$ and usually contained $MgCl_2$ as the rare-earth oxidant in an amount slightly in excess of that required for oxidation of cerium (a stand-in for all rare-earth elements). The metal charge, which simulates a discharged plutonium fuel, has been a uranium–10% plutonium–10% fissium–0.5% cerium alloy. In experiments to date,[16] about 700 g of metal and 200 g of salt have been employed. In a run without $MgCl_2$, 0.05% of the plutonium was vaporized; 0.09% was extracted into the flux. With a flux consisting of 81 wt.% $BaCl_2$–19 wt.% $CaCl_2$ to which was added 110% of the theoretical amount of $MgCl_2$, 98% of the cerium was extracted in 1 hr at 1150°C into the flux along with only 0.45% of the plutonium.[16] The resulting cerium-plutonium separation factor is about 7000. About 0.001% of the plutonium was vaporized. High-density pressed-and-sintered beryllia crucibles have been used in these tests and have performed very well, having been reused several times without evidence of failure. The high removal of cerium and the good retention of plutonium in the metal phase are evidence that this is a promising melt-refining technique, and it is being tested further.

Castleman of BNL is engaged in a program of identifying and studying the behavior of fission products released from molten uranium and uranium alloys. Although the primary purpose of the program is to develop information that will be useful in reactor safety analyses, the release of fission products from molten uranium is also pertinent to melt refining. In studies to date, attention has been given predominantly to iodine behavior because of the physiological hazards associated with ^{131}I.

In recent reports,[2,20] Castleman, Salzano, and Chandrasekharaiah discuss the release of iodine into helium, air, and steam from molten uranium and a molten uranium–3.5 wt.% molybdenum alloy previously irradiated to between 3×10^{14} and 5×10^{19} neutrons/cm^2. Most of the iodine released into helium between 1150 and 1250°C condensed in a zone having a temperature between 250 and 350°C, where elemental iodine would not condense. At temperatures above 1800°C, the iodide was partly dissociated to elemental iodine. Cesium was collected largely in a higher temperature region (600 to 900°C), and no other fission products consistently deposited with the iodine. Uranium was detected in the iodine deposition zone; however, a definite uranium-to-iodine ratio was not established. On the basis of these studies and theoretical predictions, the authors believe that the deposit is a uranium iodide, probably UI_2. They gave as further evidence the fact that iodine was slowly released from the iodine deposit upon exposure to air at 250 to 350°C. Release of iodine from CsI into air at these temperatures would not be expected. The deposition of iodine as a uranium iodide seems somewhat at variance with the work of Chellew,[21] who found that most of the cesium and iodine were deposited together in a zone having a temperature of 450 to 1000°C; Chellew therefore postulated that iodine was being deposited as CsI. However, the difference in these results may possibly be accounted for by the fact that the ratio of cesium to iodine was much higher in Chellew's experiments than in those of Castleman and Salzano.

In other experiments,[2,20] Castleman, Chandrasekharaiah, and Salzano found that elemental iodine was released from irradiated uranium heated to 1200°C in air. In steam (i.e., in a reducing atmosphere since hydrogen is formed by the reaction of steam with molten uranium), greater than 90% of the iodine was collected as iodide. Results were also reported on the adsorption of iodine on various graphites as a function of graphite temperature.[20] French workers have reported on the trapping of iodine by active charcoal.[22]

Methods of handling molten uranium are related to the technology of melt refining. In an electrolytic process under development at the Mallinckrodt Chemical Works for production of uranium from uranium oxides or scrap uranium metal,[23] uranium is produced as a molten pool under a molten fluoride electrolyte. Continuous operation is a desired feature of this process, and therefore a method of removing molten uranium and casting it into molds is considered essential. Two methods appear suitable:[24] a stopper rod and weir system using a UO_2-impregnated graphite stopper rod (see Fig. III-3) and a vacuum-withdrawal system using a heated graphite pipe to carry the molten uranium to an evacuated mold chamber (see Fig. III-4). The vacuum-withdrawal system was concluded to be the superior procedure. In laboratory tests of the vacuum-withdrawal method, up to 16 successive pours of 3.3 kg each were made, and lift heights of 23 in. (nearly the theoretical maximum) were attained.[24] Average pour time was 11 sec. In pilot-plant tests of the vacuum-withdrawal technique, 36 uranium transfers (as much as 660 lb per transfer) were made at rates of 110 to 205 lb/min and at transfer temperatures[24] of about 1300 °C. The vacuum-

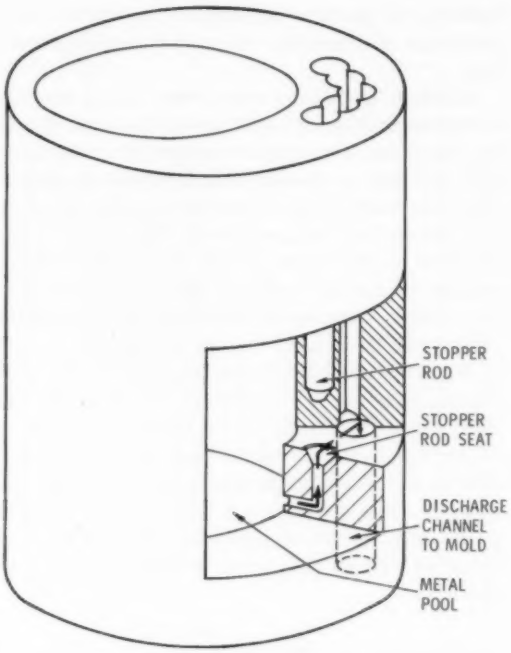

Fig. III-3 Pilot-plant stopper rod and weir crucible.[24] The uranium flow is indicated by arrows.

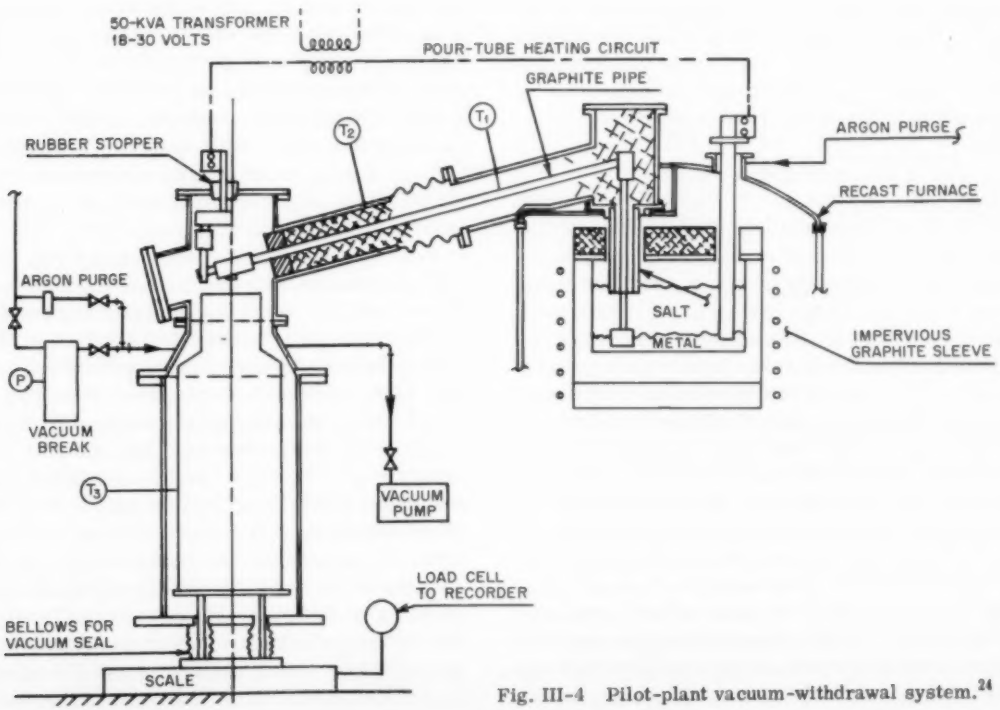

Fig. III-4 Pilot-plant vacuum-withdrawal system.[24]

withdrawal system is being incorporated into a prototype electrolytic cell now under construction.

Bunshah and Juntz have described a vacuum induction melting method (in which a crucible is not used) and a casting technique for consolidation of reactive metals without contamination.[25] The procedure involves supporting the metal on a water-cooled copper stool. The metal is restrained at the sides by the pinch effect of opposing electrical currents and assumes a conical shape. Various in-place and bottom casting techniques were used to cast the metals.

An induction-heated casting facility for plutonium has been described by Merker and Bloomster.[26] The furnaces have capacities of 25 to 500 lb of aluminum and are located in a 300-cu ft inert-atmosphere glove box. Thermal reactor fuels containing a total of over 80 kg of plutonium, including plutonium with ^{240}Pu contents as high as 20%, were processed through the facility.

Purification of Metals by Other Melting Techniques

Russian workers Kolchin, Berlin, and Presnetsova subjected samples of titanium, zirconium, and vanadium to induction zone melting.[27] Although considerable purification of these metals occurred, they ascribed it to volatilization of impurities rather than to collection of impurities at the ends of the zone-refined samples.

At Ames Laboratory three methods have been investigated for the purification of vanadium:[28] (1) electron-beam melting, (2) vacuum distillation, and (3) arc zone refining. Contrary to the above Russian results, nitrogen, iron, and nickel were removed in the direction of zone travel, but a decrease in the oxygen content was attributed to volatilization. Zone refining of thorium and yttrium by electron-beam melting was also investigated at Ames. Nitrogen and carbon in thorium moved counter to the zone, whereas uranium moved with the zone. Zone refining of thorium was concluded to be very slow and tedious and will be used only if no other methods can be found. In contrast, purification of yttrium by arc zone refining was concluded to be promising. Work has begun at Ames on the application of an electric field across the molten zone of a zone-refining apparatus in an attempt to increase the effectiveness of the zone-refining process.

An electron-beam floating-zone melting furnace has been described by Sell and Grimes of the Westinghouse Electric Corp.[29]

Fundamental Information

Lord of England has presented a review of the major physical properties of plutonium.[30] Several properties of rare-earth metals are reported in a recently issued annual summary report of the Ames Laboratory.[28]

Johnson and Leary of Los Alamos have studied phase equilibria in the Pu-$PuCl_3$ system[31] up to 1180°C. A salt-rich eutectic was found at 7 mole % plutonium and 740°C. The metal-rich eutectic is above 99 mole % in plutonium. No evidence for a plutonium halide other than $PuCl_3$ was found.

Development of Liquid-Metal and Salt Processes

Several pyrometallurgical processes are under development in which molten metals and molten salts are used as solvent media for the reactor fuel materials. Separations are achieved by selective precipitation of certain elements and by selective oxidation and reduction reactions and resultant extraction of the reduced or oxidized species into metal or salt phases. Work has been continued[15,16] at ANL on the development of a process for the recovery and purification of fissionable material in melt-refining crucible residues (skull material). A description of this process and an assessment of its capabilities have been provided in a recently issued report.[17]

A brief laboratory study[19] has been shown that stainless-steel-clad pins of the first EBR-II core which cannot be declad because of excessive radiation damage and which, therefore, cannot be melt refined can be accommodated in the skull reclamation process. The type 304 stainless-steel cladding is readily dissolved in zinc, as is the contained fuel material. The uranium may be subsequently transferred from the metal phase to a molten halide salt phase by oxidation to the trichloride by zinc chloride. Uranium may also be recovered from other nonsoluble or slightly soluble cladding materials by a "chop-leach" procedure. In a demonstration of this, tungsten-clad pins were chopped into small segments, and the uranium was dissolved out of each segment by zinc.

Work has also been continued at ANL on an extraction process for uranium-plutonium fuels in which separation of fission products from uranium and plutonium is effected by equilibrations of the fuel constituents between liquid-metal and molten-salt solvents.[15,19] The liquid-metal phase is a cadmium-magnesium-zinc alloy; the salt phase will be a LiCl-KCl-$MgCl_2$ or a LiCl-NaCl-$MgCl_2$ mixture. If cadmium is included in the metal solution, the corrosion rate is reduced to an extent that stainless steels may be satisfactory container materials.

Under investigation at Ames Laboratory has been the separation of ^{233}U from thorium by pyrometallurgical methods.[28] The experimental work has been directed to processing of thorium blankets containing about 1% uranium. In recent studies[28] aluminum has been employed as a solvent, and thorium–1% uranium alloys have been dissolved in it to about 25 wt.%. Attempts have been made to oxidize uranium preferentially and extract it into a molten-salt phase. Results obtained with LiCl and NaCl-KCl salt baths, together with $ThCl_4$, $MgCl_2$, or $FeCl_3$ used as oxidizing or complexing agents, were not encouraging. With KCl-$AlCl_3$ mixtures, however, interesting results were obtained: the oxidation of uranium at 725°C was strongly dependent on the ratio of $AlCl_3$ to KCl, whereas the oxidation of thorium was affected less by this ratio (see Fig. III-5). The sharp dependence of uranium extraction on the $AlCl_3$-KCl ratio had previously been reported by Moore and Lyon of Hanford,[32] but they did not investigate the behavior of thorium nor its effect on uranium extraction. The data shown in Fig. III-5 indicate that very good separation of thorium from uranium can be achieved. Although the extraction procedure involves extracting the major component (thorium) away from the minor component (uranium), it appears that the required separation could be achieved in about two countercurrent stages. Both phases would then have to be processed further for removal of fission products and recovery of the thorium and uranium.

Work has also been continued at Ames Laboratory on the purification of thorium by equilibrations between zinc and the KCl-LiCl eutectic salt phase.[28] Oxidation of thorium dissolved in the zinc and its transfer to the salt as $ThCl_3$ can be achieved with $ThCl_4$. This oxidation can also be achieved with a $ZnCl_2$ oxidant, and, through differences in distribution-coefficient

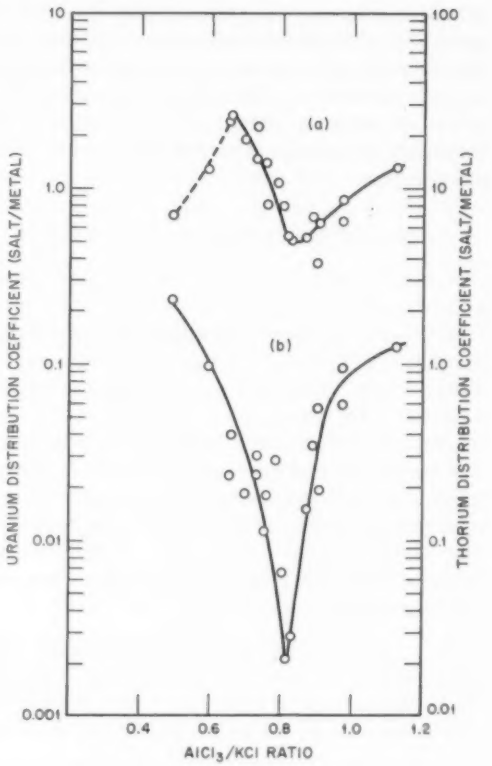

Fig. III-5 Distribution coefficients of (*a*) thorium and (*b*) uranium between KCl-$AlCl_3$ and Al vs. the equilibrium $AlCl_3$/KCl ratio.[28]

values, uranium and thorium can be separated by countercurrent extraction techniques.[28] The reactions of UC and ThC in the zinc/KCl-LiCl system are also under study at Ames Laboratory.

Equipment Developments

A low-temperature (225°C maximum) molten-salt–molten-metal extractor has been built of glass and Teflon to study the mechanics of continuous countercurrent extraction.[28] The extractor has been operated with mercury and a molten salt with no solute present. Extraction runs with a solute are now in progress. Other salt-metal systems will also be investigated.

Preliminary development work has been reported on an eddy-current induction probe for remote determination of molten-metal levels and possibly molten-salt levels.[16,19] The probe consists of dual-wound, primary and secondary Nichrome coils on a ceramic core. The output

of the secondary is strongly affected by the presence of a surrounding conductor, such as a liquid metal. A particular advantage of the eddy-current induction probe is that it operates within a well similar to a thermocouple well and may therefore be easily removed for repair or replacement.

Preparation of Metals by Reduction of Their Compounds

Reactive metals, such as thorium, uranium, and plutonium, are generally produced by electrolytic or chemical reduction of their halide salts which are often dissolved in other halide salts. These reduction procedures are closely related and are often used in pyrometallurgical processes for reactor fuels. The preparation and purification of various metals related to nuclear energy programs are discussed in the Annual Summary Report of the Ames Laboratory.[28] The metals whose preparation is being studied include vanadium, niobium, thorium, yttrium, and chromium.

The direct reduction of PuO_2 by a magnesium-zinc solution in the presence of a $CaCl_2$-$MgCl_2$-MgF_2 flux has been reported.[19] In a demonstration experiment, 30 g of plutonium metal, representing a product yield of 99%, was produced. The product was recovered by separating the flux and retorting the zinc-magnesium-plutonium ingot. Spectrochemical analyses of the product plutonium metal showed it to contain a lower level of impurities than was present in the PuO_2 starting material.

Johnson and Leary of Los Alamos have reported the first preparation of americium metal on a microscopic scale.[33] A total of 22.5 g of americium was prepared in three reductions of AmO_2 with lanthanum. The average overall yield of americium was 74%.

The reduction of rare-earth oxides with alumium to form aluminum–rare-earth alloys has been reported by Podergin and Samsanov of Russia.[34] The alumina-thermal reductions yielded aluminum alloys containing up to 30 to 50% of rare earths.

A patent by Domning has been assigned to the Dow Chemical Co. on the production of cerium by reduction of its chloride by sodium or barium at about 400°C (Ref. 35). The salt-metal mixture is subsequently heated to about 740 to 760°C to melt the cerium, which is then removed from the salt phase (which is still solid), by filtration.

Information on the availability of high-purity metals and their sources in America has been compiled by Wilhelm and McCarley of Ames Laboratory.[36] The production, preparation, and properties of pure metals have also been discussed in a series of recorded lectures.[37]

Fundamental Studies Relative to Liquid-Metal Process Development

A broad base of fundamental information is required for the logical design of pyrometallurgical processes and for sound interpretation of process phenomena.

Thermodynamic Data

Phase diagrams are important for an understanding of phenomena in liquid-metal systems used in pryometallurgical processes. The thermodynamic properties and phase equilibria in numerous alloy systems are under study at Ames Laboratory. Of particular interest to pyrometallurgical processes are studies reported in the Annual Summary Report of Ames Laboratory on the cerium-zinc and thorium-magnesium systems.[28] The identification of compounds in the cadmium-lanthanum system and thermodynamic data for these compounds have recently been reported by ANL.[15,16]

Engineering Data

Vaporization from the liquid plus vapor surface of a liquid-metal pool without the formation of vapor bubbles (called nonturbulent vaporization) is a method of vaporization that is of interest for liquid-metal evaporation and retorting steps of pyrometallurgical processes, since very little entrainment occurs. This type of vaporization is being studied with mercury at ANL.[15,19] A steep and constant temperature gradient as high as 115°C/in. has been found in a thin surface layer (about 0.2 in. thick). The temperature of the vaporizing surface has been found to be superheated an average of 30°C above the vapor space saturation temperature at vaporization rates equivalent to between 64,000 and 115,000 Btu/(hr)(sq ft of liquid surface).

A small forced-convection loop containing a flash distillation chamber has been employed by Burnet and Westerheide of Ames Laboratory to study the separation of liquid metals by flash distillation.[28] The loop has been operated with a lead-bismuth eutectic containing 10% cadmium

as the volatile constituent. After a single pass of alloy through the chamber, the condensate was as high as 99% in cadmium. In continuous operation, enrichment of the vapor in cadmium with efficiencies of 60 to 70% of theoretical was realized.

A simple apparatus for obtaining vapor-liquid equilibria in metal systems has been constructed at Ames Laboratory and has been used to obtain activity coefficients for the bismuth-cadmium system.[28]

Various liquid-metal boiling studies, which are principally associated with alkali metals, are reviewed in the fifth of a series of liquid-metal technology reviews.[38]

Construction Materials for Liquid-Metal Fuel or Liquid-Metal Process Systems

A major objective of the Los Alamos Molten-Plutonium Reactor Experiment (LAMPRE) is the evaluation of container–plutonium-fuel-alloy combinations in a reactor environment. Tantalum capsules have been used in core I and core II loadings of the LAMPRE reactor for containment of plutonium–10 at.% iron fuel alloy. The severe corrosion of the core I and core II capsules and the fact that significant improvements in materials are not now available led to a decision to postpone indefinitely the planned third loading of the LAMPRE reactor.[39] Instead, increased emphasis will be given to out-of-reactor corrosion tests. Any in-reactor corrosion tests will be performed in another reactor, the Omega West Reactor (OWR).

All core II capsules are being subjected to a detailed examination.[39] Examinations made to date indicate that weld areas are most susceptible to intergranular penetration. In out-of-reactor tests, both double-arc-melted tantalum and electron-beam-melted tantalum capsules have exhibited good corrosion resistance to the plutonium-iron fuel alloy at 600°C. A tantalum–0.1% tungsten alloy has performed poorly. All capsules made of this latter material failed within 700 hr in out-of-reactor tests at 650 and 700°C. Internally carburized tantalum capsules survived 4200 hr of test at 600°C without evidence of leakage, but one capsule failed in the vapor region after 4200 hr at 650°C.

Work is also continuing at Los Alamos in two other areas:[39] (1) the evaluation of tantalum for the containment of liquid plutonium-cobalt-cerium alloys and (2) the investigation of several methods of joining tantalum (percussion and projection welding and diffusion bonding).

Corrosion work in liquid-metal systems has been received by Dwyer.[38] Progress reports by Argonne,[15,16,19] Ames,[28] and Brookhaven[2] laboratories also contain information on the corrosion of various materials by liquid-metal alloy systems. (L. Burris)

Other Nonaqueous Processes

Processes utilizing dry, high-temperature chemical conversions are being developed for the recovery of fissile and fertile materials from irradiated oxide and carbide reactor fuels. Gases, molten salts, and liquid metals are generally employed as reagents and process media. Since these materials are not susceptible to radiation damage, processes of this type are particularly suited to closed, low-decontamination, remotely operated cycles for short-cooled high-burnup fuels.

Oxide Fuel Processing

Development work has continued at Hanford on the salt-cycle process, a closed-cycle process for uranium dioxide–plutonium dioxide fuels associated with the Plutonium Recycle Test Reactor (PRTR).[40–43] In the salt-cycle process, the fuel is first declad mechanically and then oxidized in air at about 450°C to convert the uranium dioxide to uranosic oxide, thereby pulverizing the material. The mixed oxide powder is then dissolved in a chloride melt such as LiCl-KCl by sparging the system with a mixture of chlorine and hydrogen chloride. Two general methods have been developed for the recovery of uranium and plutonium oxides from this solution. One, the subject of a recently issued patent,[44] involves selective electrodeposition of essentially plutonium-free uranium dioxide on a graphite cathode in an oxygen-free atmosphere. The uranium remaining in the melt is then codeposited electrolytically together with the plutonium to form a solid solution of uranium dioxide and plutonium dioxide. This latter electrodeposition step, which is conducted with an oxygen-chlorine sparge, results in an oxide mixture that may be considerably enriched in

plutonium. The other general method of separating and recovering the uranium and plutonium involves selective precipitation of the plutonium as the dioxide by sparging the melt with an oxygen-chlorine mixture. Essentially plutonium-free uranium dioxide is then electrodeposited from the melt.

In engineering development studies of the salt-cycle process, three electrodeposition runs were performed in a High-Level Radiochemical Facility, using a LiCl-KCl melt in which unirradiated uranium oxide–plutonium dioxide mixtures had been dissolved by chlorine and hydrogen chloride sparging.[40–42] The conditions of these runs are listed in Table III-3. Although

Table III-3 CONDITIONS OF CODEPOSITION OF URANIUM DIOXIDE AND PLUTONIUM DIOXIDE[40,41]

(Salt Bath: LiCl-KCl)

Run No.	1	2	3
Initial concentration in melt			
Uranium, wt.%	27	18	17.2
Plutonium, wt.%	0.18	0.17	0.068
Temp., °C	550	555	550
Sparge gas			
Oxygen, liters/min	1	1.8	1.8
Chlorine, liters/min	1	0.2	0.2
Electrodeposition conditions			
Potential, volts	1.7	1.65	1.40
Initial current density, amp/cm^2	0.19	0.18	0.19
Current efficiency, %	66	78	66
Weight of electrodeposited product, lb	14	16.9	9.8

the plutonium-to-uranium ratios in the products were somewhat lower than the starting ratios in the melts, it was shown that uranium oxide–plutonium dioxide mixtures can be codeposited. The oxygen-to-uranium ratio of the product was between 2.000 and 2.005 on the average; when the product was washed with water, the chloride content was decreased to the range of 28 to 50 ppm. A fourth electrolysis at a higher voltage was used to clean up the bath. Operations with irradiated fuels have been started in the same facility.[42] Two mixed-oxide fuel assemblies containing 0.45% plutonium in natural uranium were irradiated in the PRTR. One was irradiated to 100 Mwd/ton and cooled for 292 days; the other was irradiated to 360 Mwd/ton and cooled 373 days. Vibratory decladding of fuel rods and partial oxidation of the uranium dioxide to uranosic oxide were successfully demonstrated, and the resulting oxide mixture was dissolved in the salt bath by sparging with chlorine.

Further chemical studies pertaining to the salt-cycle process have also been reported. Equilibrium constants (concentrations in molarity) for the reaction

$$UO_2Cl_2 + UO_2 \rightleftharpoons 2UO_2Cl$$

in the LiCl-KCl eutectic have been determined:[40]

Temp., °C	K
500	0.0016
600	0.0050
700	0.013

The behavior of uranium and plutonium in equimolar LiCl-KCl at concentrations (0.2 wt.% plutonium, 15 wt.% uranium) and temperatures (500 to 600°C) typical of those used in the engineering-scale demonstration runs has been investigated.[41] Equilibrium constants for the reactions

$$PuO_2Cl_2 \rightleftharpoons PuO_2Cl + \tfrac{1}{2}Cl_2$$

$$PuO_2Cl \rightleftharpoons PuO_2 + \tfrac{1}{2}Cl_2$$

proved to be such that only about 0.1 wt.% plutonium is stable in this system as plutonyl ion, even at a chlorine partial pressure near 1 atm. However, because the rate of plutonium dioxide precipitation from solutions containing larger concentrations of plutonyl ion is slow when the melt is sparged with oxygen-chlorine mixtures, it is possible to maintain plutonyl concentrations greater than the equilibrium values for some time. Plutonium dioxide is precipitated rapidly if chlorine is removed from the melt by sparging with helium. Measurements of the oxidation rates of U(IV) and Pu(IV) in melts sparged with oxygen-chlorine mixtures showed that the uranium oxidation rate was about twice that for plutonium. Changing the temperatures from 500 to 600°C resulted in approximately a fourfold increase in both the oxidation rates. The oxidation rates appeared to be more dependent on the partial pressure of oxygen in the sparge gas than on the oxygen flow rate. When both U(IV) and Pu(IV) were present in the melt, oxidation of the plutonium did not begin until the uranium had been oxidized.

Additional measurements of electromotive force have been made on the reaction

$$Ni + Cl_2 \rightleftharpoons NiCl_2$$

in an effort to examine the general effect of melt composition on electromotive force.[41,42] Measurements were made in the following solvent systems of varying composition: LiCl-KCl, NaCl-KCl, and LiCl-NaCl. Plots of the electromotive force vs. the mole% concentration of NaCl or KCl in the solvent were nearly straight lines. In the LiCl-NaCl system, Ni(II) did not exhibit the titration type curve observed for uranyl(VI) ion. The slopes of the electromotive-force composition curves for Ni(II) in the three solvents increased in the order LiCl-NaCl, NaCl-KCl, and LiCl-KCl, whereas the uranyl(VI) solutions showed slopes increasing in order of increasing chloride activity, i.e., LiCl-NaCl < LiCl-KCl < NaCl-KCl.

Work is also being carried out at Hanford on a ^{233}U-thorium fuel cycle.[42] The dissolution rate of thorium dioxide in a LiCl-KCl melt sparged with hydrogen chloride proved to be low, but addition of 37.5 mole% CsCl to the melt appeared to increase both the rate and extent of dissolution. A thorium concentration of 10 wt.% in the melt was achieved after 24 hr of sparging with hydrogen chloride. Both selective electrodeposition of uranium dioxide and selective reduction of uranyl chloride with hydrogen are receiving consideration as potential methods for the separation of uranium from thorium.

European studies of separation processes involving electrodeposition and chemical precipitation of uranium dioxide from molten chloride solvents have also been reported.[45,46] In connection with chlorination procedures for fuel processing, the uranium dioxide precipitation technique has resulted in uranium-cesium purification factors amounting to 2 orders of magnitude.[45] Uranium dioxide has been prepared by chemical precipitation from LiCl-KCl and NaCl-KCl at 600 to 650°C (Ref. 46). Uranium tetrafluoride was added to the melt, which was sparged with oxygen and then with argon to remove the residual oxygen. The uranium dioxide was then precipitated by sparging with hydrogen for 3 to 5 hr. In the later tests, the uranium dioxide produced had a 2.01 ratio of oxygen to uranium and 98% of the theoretical density. Work is continuing in an effort to improve the yield and quality of the product.

Gaseous Low-Decontamination Process for Uranium Dioxide Fuels

At Atomics International a development effort is continuing on the AIROX process for uranium dioxide fuels.[47–50] This process consists of decladding and pulverizing the fuel by alternate oxidation with air or dilute oxygen at 200 to 600°C and reduction with hydrogen at 600°C. The powdered uranium dioxide product is reenriched by blending and is then refabricated by cold pressing and sintering. Fuel pellets made from irradiated uranium dioxide (5700 to 15,000 Mwd/metric ton), which had previously been processed and refabricated, have been reirradiated in the MTR. Preparations are being made for postirradiation examination and processing of this material. Mockup studies are in progress, and construction and installation of remotely operated equipment in a cave facility have continued.[47–50]

Carbide Fuel Processing

At Atomics International the main emphasis on low-decontamination procedures for the recovery of uranium carbide fuels is being placed on the CARBOX process.[47–50] In this process, low-temperature oxidation of the carbide by air, oxygen, or steam is used to form uranium oxide. The oxide is then reconverted to uranium monocarbide by carbothermic reduction at a temperature of about 1500°C. Although arc melting was initially chosen as the primary refabrication procedure, losses of plutonium by volatilization during arc melting have led to consideration of other methods.

Scale-up studies have continued on the oxidation of kilogram quantities of uranium monocarbide in a controlled-atmosphere rotary furnace. Three 5-kg batches and one 7-kg charge of cast uranium carbide were oxidized in flowing air (40 to 50 cu ft/hr) at atmospheric pressure. Finely divided U_3O_8 was produced; most of the product was a −200-mesh fraction that was suitable for reconversion to the carbide.[48,50] Several subsequent oxidations were conducted using charges of 3 to 10 kg of uranium monocarbide.[49,50] This material consisted of slugs (carbon content, ~4.64 wt.%) which had been activated by exposure to water vapor at temperatures up to 80°C. The oxidation was performed at 500°C in flowing air, and the temperature was then raised to 550°C for 1 hr. Nearly all the material was converted to oxide,

and 50 to 90% of the product was in the −200-mesh size range. The activation effect aided in achieving complete oxidation of the carbide. It was found that an internal filter could be freed of uranosic oxide deposits by reversing the air flow. Use of this technique permitted an air flow rate of about 70 cu ft/hr, which corresponds to a theoretical oxidation rate of approximately 2 kg/hr. Evaluations of the product fractions from one run indicated that the small amounts of unreacted uranium monocarbide in the product appear mainly in the coarser fractions. Further experiments were conducted in which an attempt was made to decrease the proportion of coarser fractions of the uranosic oxide product by lowering the oxidation temperature. It appears that the optimum oxidation temperature in this respect may be in the vicinity of 450°C.

Scale-up studies on the carbothermic reduction of U_3O_8 have also continued.[47–49] Investigations were conducted on the carbon contribution from the binder (polyvinyl alcohol) used to prepare the pellets and on the reduction when hypostoichiometric (in carbon) uranium monocarbide is prepared. (Difficulty was encountered in obtaining complete reduction during the preparation of hypostoichiometric uranium carbide, but the reaction went to completion readily when hyperstoichiometric material was prepared.) It is believed that variables associated with the batch size and furnace geometry may contribute to this effect.

Laboratory-scale studies of the preparation of uranium monocarbide by sintering pellets of mixed U_3O_8 and carbon have continued. Density determinations were made on pellets that had been sintered for 5 hr at 1750°C (Ref. 47). The pellets themselves had densities ranging between 11.32 and 11.76 g/cm^3. Powders produced by crushing the pellets to a size range suitable for vibratory compaction gave density values from 12.24 to 12.72 g/cm^3. Small additions of sintering aids such as iron, nickel, alumina, or intermetallic compounds to the uranosic oxide–carbon pellets resulted in slight increases in the density of the product.[48–50] A few typical data are listed in Table III-4. These results indicate that UAl_2 and UFe_2 were the most effective additives.

The possibility of forming microspheres from uranium monocarbide powder by means of a plasma torch is under study.[48,50] Spheres of good appearance have been produced from particles of less than 100 mesh.

Two experiments have been performed to determine whether uranium monocarbide will react with hydrogen under pressure in a temperature region where uranium hydride is stable.[47] Arc-melted specimens of the carbide having carbon contents of 4.6 and 5.05 wt.% were heated to 500°C in a stream of hydrogen at 15-atm pressure. Little or no hydrocarbon was formed, and the individual uranium carbide showed no evidence of reaction.

Table III-4 EFFECT OF ADDITIVES ON DENSITY OF URANIUM MONOCARBIDE PELLETS[48–50]

(Maximum Sintering Temperature, 1750°C)

Additive			UC density, g/cm^3	
Material	At.%	Wt.% C	Pellet	Crushed material
Fe	1	4.73	10.88	12.73
Ni	1	4.71	11.62	12.72
Al_2O_3	1	4.61	12.04	12.52
UAl_2	1	4.58	11.35	12.84
UFe_2	1	4.69	11.56	12.85
UNi_2	1	4.72	11.25	12.72

A topical report[51] has been issued on small-scale studies of the behavior of plutonium and fission products at high temperatures (particularly during arc melting) in the CARBOX process. Since arc melting was the first method of refabrication considered for carbide fuels at Atomics International, the possibility of plutonium losses by volatilization during arc melting was of special interest. It is desirable to retain plutonium in the recycled fuel to offset the effects of fission-product poisons and ^{235}U consumption.

Uranium dioxide powder was irradiated at a flux of 10^{19} neutrons/(cm^2)(sec) and cooled for five years. The plutonium content was about 35 ppm. The other important activities were ^{90}Sr-Y, ^{106}Ru-Rh, ^{137}Cs-Ba, ^{144}Ce-Pr, and ^{147}Pm. Three oxidation-reduction cycles (oxidation with air at 400°C; reduction with 85% nitrogen–15% hydrogen "forming gas" at 650°C) were used to pulverize the somewhat sintered material. The oxide was blended with −400-mesh graphite, pelletized, and heated as follows: 1 hr at red heat; 2 hr at ~1100°C; 2 hr at ~1560°C; and 3 hr at 1560, 1760, or 1940°C. Three different proportions of oxide and graphite were used so as to produce hyperstoichiometric, stoichio-

metric, and hypostoichiometric uranium monocarbide as follows:

Mixture	C : UO_2 mole ratio	Calculated carbon content, wt.%
H	3.17	5.57
M	3.00	4.80
L	2.88	4.25

In addition to the heating schedule described above, one pellet each of the H, M, and L mixtures was arc melted.

The results of this study are summarized in Table III-5. The loss of plutonium was substantial, except at the lowest temperature, and was nearly complete on arc melting. Cerium behaved similarly, suggesting its possible use as a stand-in for plutonium in inactive experiments. The extent of plutonium and cerium vaporization increased with decreasing carbon content, as might be expected in the case of elements that form carbides. Both cesium and and strontium were almost completely removed in all the runs.

In a separate experiment, irradiated uranium carbide with a carbon content of 5.2 to 5.5 wt.% and a plutonium concentration of 0.7 ppm was arc melted. Plutonium and fission-product removals were Pu, 40 to 66%; Ce, 57 to 71%; Cs, 96 to 99%; Zr-Nb, 0 to 4%.

The large plutonium losses at these low concentrations do not necessarily indicate that proportional losses will occur at high concentrations. For instance, it is possible to prepare uranium carbide–plutonium carbide alloys by oxide reduction. However, large plutonium losses are incurred during arc melting. It appears that arc melting cannot be used satisfactorily either in the processing of uranium carbide fuels or in the initial fabrication of mixed uranium-plutonium carbide fuels.

Table III-5 CARBOTHERMIC REDUCTION OF IRRADIATED URANIUM DIOXIDE[51]

(Conditions: See Text)

Mixture	Max. temp., °C	Percent removal			
		Pu	Ce	Cs	Sr
H	1560	6	22	97	98
H	1940	17	30	99	100
H	Arc melted	80	84	100	100
M	1560	6	14	97	98
M	1940	33	44	99	100
M	Arc melted	94	97	100	100
L	1560	14	17	98	98
L	1760	38	37	99	99
L	1940	46	71	99	100
L	Arc melted	98	98	100	100

Oxidation of Uranium Carbide and Oxide

Two European studies of the oxidation of uranium monocarbide by gaseous reagents have been reported.[52,53] In an investigation employing differential thermal-analysis techniques,[52] oxidation rates of uranium monocarbide were determined in air and oxygen atmospheres. The reaction was strongly exothermic and occurred at about 350°C. By careful control of the conditions, U_3O_8 could be obtained as the sole product. A study of uranium monocarbide oxidation by carbon dioxide in oxygen and in water vapor at temperatures of 350 to 600°C was made, using a thermobalance.[53] The initial rates were linear, but they subsequently increased because of progressive fragmentation of the samples. The presence of uranium or uranium dicarbide inclusions in the monocarbide decreased its resistance to oxidation, probably because these materials undergo rapid oxidation. The activation energy for the uranium monocarbide oxidation reaction was 29 kcal/mole.

The differential thermal-analysis technique was also used to investigate the oxidation of uranium dioxide in air and in oxygen.[52] The reaction was found to proceed in two steps: first an intermediate was formed and then U_3O_8, a result which was reported previously.[54] Oxidation of a uranium dioxide–molybdenum pellet resulted in a mixed phase, MoO_3-U_3O_8, which melted at about 1000°C. (R. K. Steunenberg)

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Section

IV

Reactor Fuel Processing

Waste Disposal

Vienna Symposium on the Treatment of High-Level Radioactive Wastes

A symposium on the treatment and storage of high-level radioactive wastes was held in Vienna, October 8–12, 1962, under the auspices of the International Atomic Energy Agency. Thirty-three papers were presented which covered management, treatment, and ultimate disposal of high-level-activity wastes. The papers and their discussions have been incorporated in the proceedings[1] of this meeting. A number of these papers are discussed in the following subsections.

Volume Reduction of Liquid Wastes by Evaporation

Murray[2] at Chalk River, Canada, has described the various evaporator installations that are or have been in use at Chalk River for a variety of radioactive liquid wastes. A pot type evaporator has been in operation since 1958 for the processing of low-level-activity wastes. The evaporator consists of a glass-lined vessel, 40 in. in diameter by 42 in. in height, to which is attached a steam-heated glass-lined column, 10 in. in inside diameter by 6 ft in height, for additional disengaging space. No deentrainment devices are employed with this evaporator. The evaporator has a throughput rate of 20 imperial gal/hr and is operated at an internal pressure of −10 in. Hg. When an antifoaming agent is added to the waste solution, instantaneous decontamination factors* up to 1×10^5 have been obtained. If no antifoaming agent is used, the carry-over of radioactivity to the distillate is excessive, and the distillate must be recycled to the evaporator for further processing.

A new pot type evaporator (see Fig. IV-1) to be constructed of type 347 stainless steel has been designed to replace the glass-lined pot evaporator. The evaporator will be 54 in. in diameter and will have a holdup volume of 200 gal. A 20-in.-diameter deentrainment column in which there are two deentrainment devices surmounts the evaporator. The first device will be an impingement plate, and the second device will be a wire-mesh demister unit. The evaporator has been designed for a throughput rate of 200 imperial gal/hr. The possibility of a violent chemical reaction occurring within the evaporator has been minimized or eliminated by providing a bursting disk (set at 10 psig) and by limiting the maximum steam pressure (and hence the solution temperature) to 30 psig. Startup operation of the evaporator was expected to take place in 1963.

A rising film type evaporator (see Fig. IV-2) is being used for the processing of high-level-activity liquid wastes and has been in operation since April 1961. The evaporator that is constructed of type 347 stainless steel is designed for a throughput rate of 22 imperial gal/hr and a volume reduction factor of 5. The evaporator tubes are in the lower portion of the evaporator. Two deentrainment devices are located in the disengaging section above the top of the evaporator tubes. The first device is a baffle plate, and the second device is a titanium wire-mesh demister located at the top of the evaporator.

*Defined as concentration of beta activity in the concentrate at any instant divided by the concentration of beta activity in the distillate at the same instant.

In initial operation with radioactive solutions, decontamination factors of about 1 to 2×10^6 were achieved at volume reductions of 2.5 to 5.

Chambon and Rodier[1,3] have described the installation and procedures for the concentration and storage of the high-level-activity aqueous wastes originating at the Marcoule (France) plant for the extraction of plutonium from irradiated natural uranium. The nitric acid effluent from the first extraction step of the plutonium recovery process which contains some 99% of the gamma activity originally present in the fuel is the principal source of the highly active wastes. The flow sheet for the processing of this waste effluent (Extraction I) is shown in Fig. IV-3. The effluent is first treated to remove entrained solvent and is then stored for at least 24 hr prior to evaporation. The concentration by evaporation is carried out in two steps at atmospheric pressure. The effluent is initially concentrated 10- or 15-fold in the first evaporator, and the concentrate is then transferred to a second evaporator for an overall concentration factor of 70 for the two evaporation steps (equivalent to 50 liters/metric ton of natural uranium). The concentrated waste is then stored as an acid ($3N$) waste in stainless-steel (type 18-8, low carbon content) tanks. Decontamination factors (gamma) of about 5×10^5 have been achieved for the first evaporation step, and overall decontamination factors (gamma) of about 1×10^6 have been obtained through the second evaporation step. During the two concentration steps, the nitric acid is maintained at $3N$ by continuously feeding formaldehyde to the evaporators. The nitrous vapors produced in the two evaporators are treated in two columns in series in which oxidation by air and adsorption by water are carried out. The off-gas, after filtration, is then discharged to the atmosphere via a stack.

Clelland[1] of the United Kingdom Atomic Energy Authority at Risley, England, has discussed how the United Kingdom expects to handle the increased volumes of highly active processing wastes which are expected to arise as a result of the expanding United Kingdom civil nuclear power program in the period 1962 to 1980. In this period an estimated 28,000 metric tons of

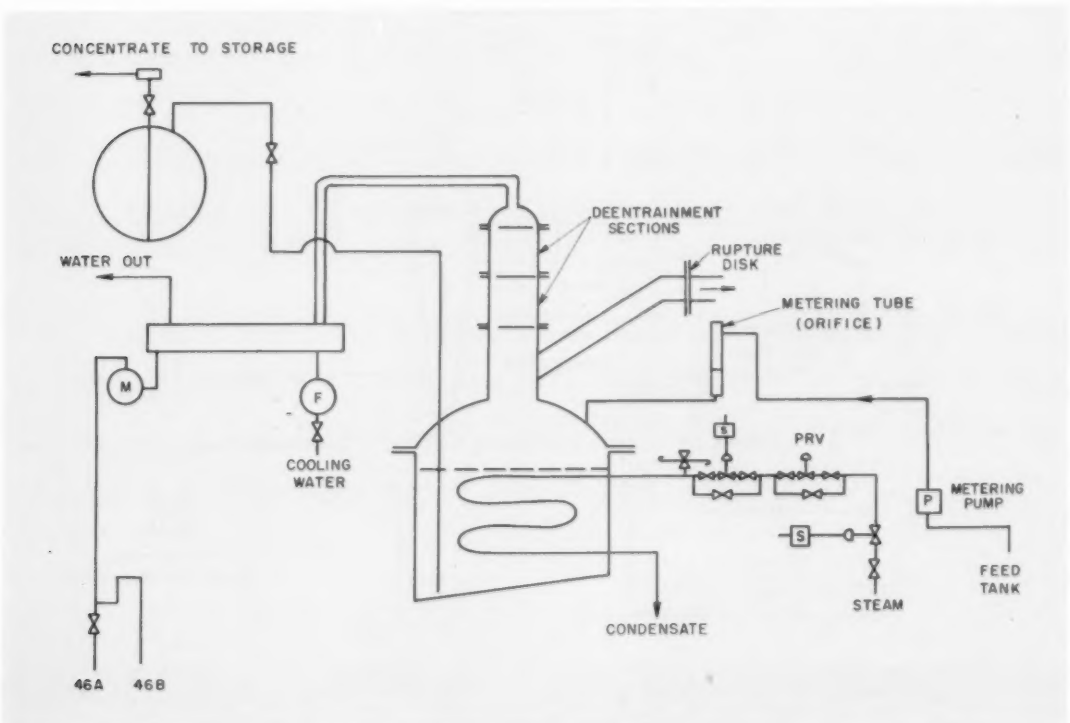

Fig. IV-1 Simplified flow sheet for low-level-activity waste effluent evaporator.[2]

irradiated uranium will be produced which will require processing. The author suggests that the present United Kingdom policy (which has been in effect at Windscale for a number of years) of concentration by evaporation (see Fig. IV-4) and storage of highly active acidic waste solutions can also be applied to the future processing of similar types of wastes.

In order to be able to handle the anticipated volume increase in high-level-activity wastes, the highly active evaporation plant at Windscale is being expanded. Two new evaporation units (see Fig. IV-5) and storage tanks of a new design (see Fig. IV-6) are being added. An estimated tank storage capacity of some 1127 m^3 will be needed to handle the highly active concentrate that will arise from the evaporation of the wastes that are expected to be produced from the processing of the 28,000 metric tons of irradiated uranium. An overall concentration of 150:1 is expected; a factor of 50:1 or 75:1 will be initially achieved in the evaporation plant followed by an additional factor of 3:1 or 2:1 in the storage tanks. (This is equivalent to a concentrate volume of 40 liters/metric ton of uranium processed.)

A jacketed kettle type evaporator is to be used and is to be constructed of stainless steel (type 18-13 Nb). In order to reduce corrosion attack, vacuum operation of the evaporator at an internal pressure of 70 mm Hg is planned. At this pressure and a design boilup rate of 25 lb/(sq ft)(hr), the throughput rate of highly active waste solution would be about 18 m^3/day.

The design of the new storage tanks will provide increased cooling capacity to handle the fission-product decay heat from evaporator concentrates of high specific activity and a means of agitation of the tank contents. The size of storage tanks may be increased in proportion to the scale of the processing programs, possibly increasing from 150 m^3 to 300 m^3 capacity. The tanks will be contained in concrete cells that will be lined with stainless-steel sheet up

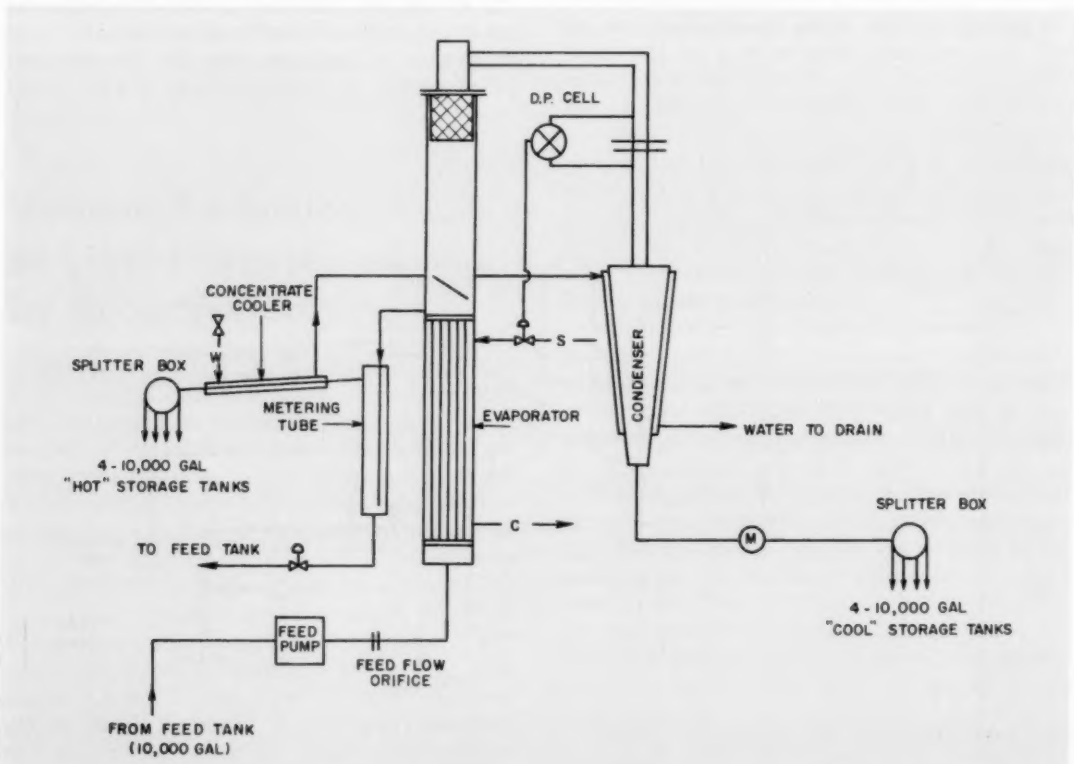

Fig. IV-2 Rising film type evaporator for high-level-activity wastes.[2]

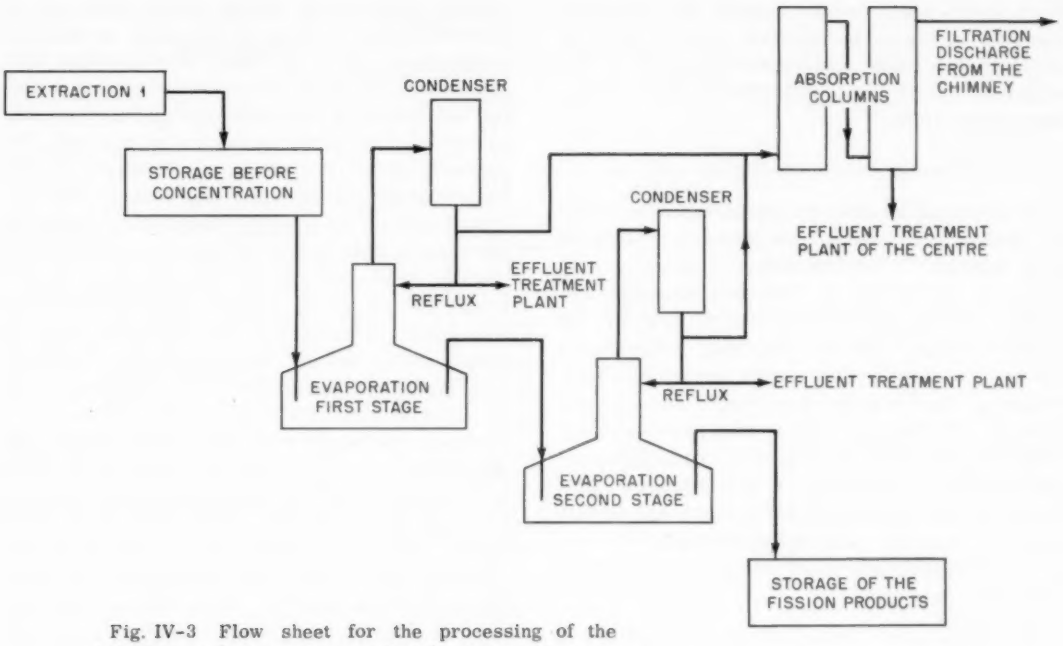

Fig. IV-3 Flow sheet for the processing of the fission-product wastes produced at the Marcoule (France) plutonium recovery plant.[3] (Reprinted with permission from the United Kingdom Atomic Energy Authority Research Group, British Translation AERE-Trans-938.)

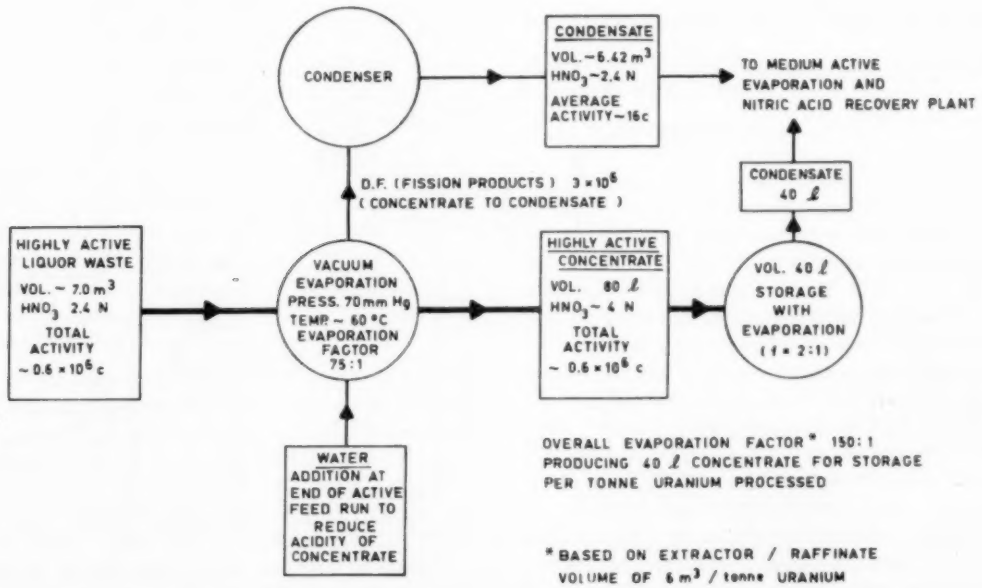
CONDENSER
CONDENSATE
VOL. ~ 6.42 m³
HNO₃ ~ 2.4 N
AVERAGE ACTIVITY ~ 1c
TO MEDIUM ACTIVE EVAPORATION AND NITRIC ACID RECOVERY PLANT
D.F. (FISSION PRODUCTS) 3 × 10⁶
(CONCENTRATE TO CONDENSATE)
CONDENSATE 40 ℓ
HIGHLY ACTIVE LIQUOR WASTE
VOL. ~ 7.0 m³
HNO₃ 2.4 N
TOTAL ACTIVITY ~ 0.6 × 10⁶ c
VACUUM EVAPORATION
PRESS. 70 mm Hg
TEMP. ~ 60 °C
EVAPORATION FACTOR 75:1
HIGHLY ACTIVE CONCENTRATE
VOL. 80 ℓ
HNO₃ ~ 4 N
TOTAL ACTIVITY ~ 0.6 × 10⁶ c
VOL. 40 ℓ
STORAGE WITH EVAPORATION (f = 2:1)
WATER ADDITION AT END OF ACTIVE FEED RUN TO REDUCE ACIDITY OF CONCENTRATE
OVERALL EVAPORATION FACTOR * 150:1
PRODUCING 40 ℓ CONCENTRATE FOR STORAGE PER TONNE URANIUM PROCESSED
* BASED ON EXTRACTOR / RAFFINATE VOLUME OF 6 m³ / tonne URANIUM

Fig. IV-4 Evaporation process for concentration of highly active wastes at Windscale.[1]

to a level which would contain the complete contents of the tank. The first of the new tanks (150 m^3) has been constructed (type 18-13 Nb stainless steel) and is expected to be in operation during 1964.

Hanford Denitration of Purex Acid Wastes with Sugar

Hanford has adopted the use of sugar (sucrose) for routine plant use for the denitration of Purex acid wastes.[4-6] Destruction of the nitric acid (from an initial 5*M* to 10*M* to a minimum residual acidity of about 0.5*M* free acid) in the waste stream has the following advantages: (1) less sodium hydroxide is needed for neutralizing the wastes for long-term alkaline storage, (2) the final volume of stored wastes is reduced, (3) recovery of fission products is improved with a reduction in the sodium content of the stored waste, and (4) the decreased acidity and the smaller processing volumes are expected to result in a more economical recovery of fission products.

Formaldehyde[6,7] was previously used in a denitration unit that was placed in operation in the Purex plant during 1962. Because of difficulties encountered during initial plant use of formaldehyde, a study of alternate methods of denitration was undertaken. The reaction with sugar is much less vigorous and exothermic than the reaction with formaldehyde and can be safely carried out in large batch-size equipment. The products of the denitration reaction are all gaseous (oxides of nitrogen and carbon). No residual carbon or organic compounds remain in the treated solutions to complicate further processing or storage. Nitric acid can be recovered from the off-gases by means of conventional downdraft condensers. The reaction rate is easily controlled by the rate of sugar addition. The threshold temperature for initiation of the reaction is about 85°C. When the reaction temperature is increased from 85 to 100°C, the efficiency of the process is improved by about 10%. However, unlike the formaldehyde process, the use of a reaction tower above the reaction vessel does not improve the overall sugar utilization efficiency. The efficiency of HNO_3 decomposition does not vary with acid concentration over the range 0.5*M* to 8*M*. The decomposition of HNO_3 does vary with the concentration of dissolved multivalent metal cations

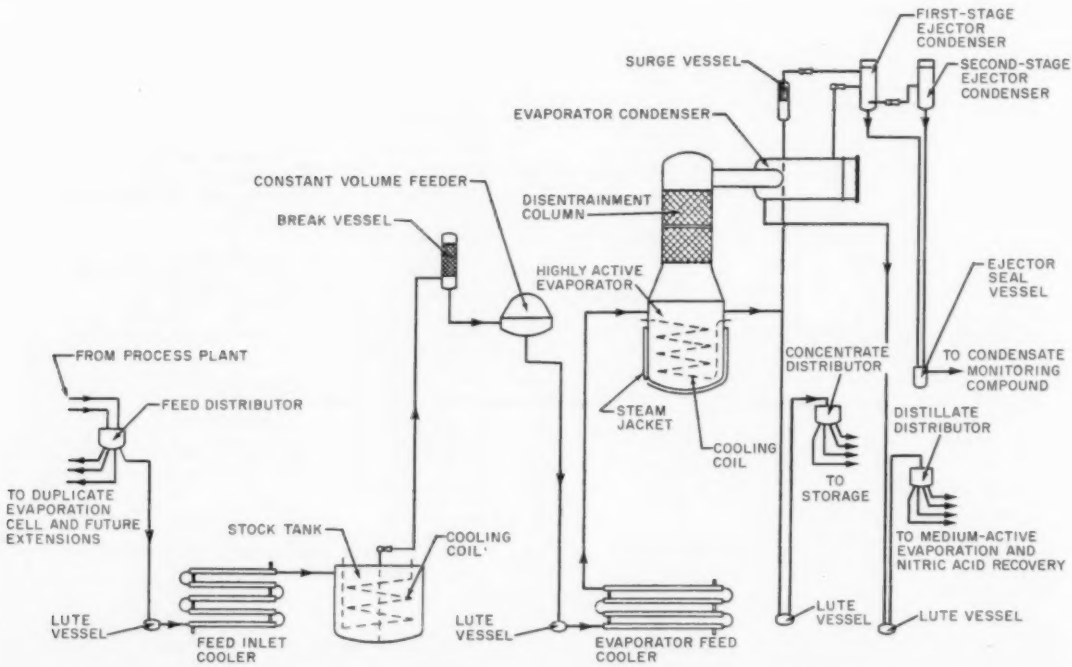

Fig. IV-5 A simplified flow diagram of the highly active evaporation plant to be installed at Windscale.[1]

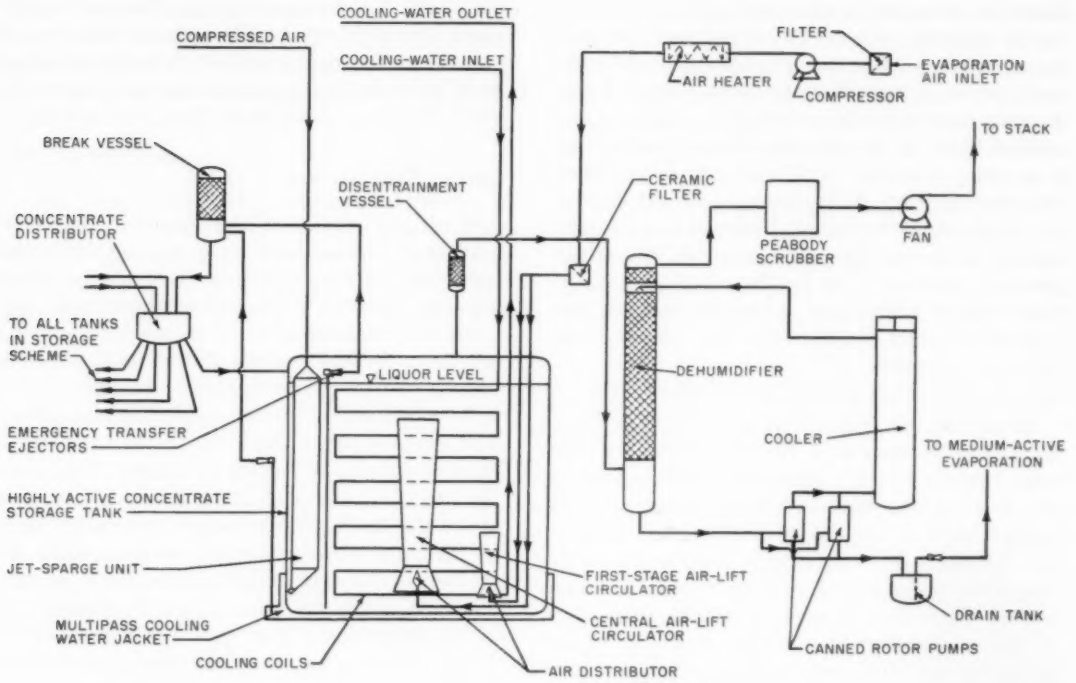

Fig. IV-6 Simplified flow diagram of new storage tank and associated equipment being installed at Windscale.[1]

(e.g., iron and chromium). Approximately 12 to 20 moles of HNO_3 are destroyed per mole of sugar fed as the iron concentration increases from $0M$ to $1M$. In the Purex plant test, which was a successful culmination of the laboratory and semiworks development program, the hydrogen concentration, initially $4.5M$, in a 2500-gal batch of full-plant-level-activity Purex waste (1WW) was reduced, after heating and slowly adding 1600 lb of sugar, to a residual hydrogen concentration of $0.68M$. This was the equivalent of 18.2 moles of HNO_3 decomposed per mole of sugar.

The economics of denitration of Purex wastes are highly dependent on the cost of sugar. At the present prices of 10 cents/lb for sugar and 4 cents/lb for 37% formaldehyde, the cost per pound of acid destroyed is 3.04 cents for sugar and 2.37 cents for formaldehyde. If molasses were used, the reagent cost would be 1.17 cents/lb of acid destroyed. In a new plant, denitration with sugar might be lower than with formaldehyde because of simpler equipment and instrumentation.

Conversion of High-Level-Activity Wastes to Solids

Fluid-Bed Calcination

AEC[8] has announced the successful demonstration of the fluid-bed calcination[9] of high-level-activity liquid wastes in the Waste Calcining Facility (WCF) at the National Reactor Testing Station (NRTS), Idaho. (The WCF is operated for AEC by the Phillips Petroleum Co.) The WCF has a design capability for processing some 1440 gal of waste solution per day. In this test run the WCF was operated continuously for eight weeks. Five-year-old wastes from the processing of enriched-uranium–aluminum alloy fuels were used as feed material to the 48-in.-diameter fluid-bed calciner in the WCF. The wastes came from one of the nine 300,000-gal waste storage tanks at the Idaho Chemical Processing Plant (ICPP), NRTS. The volume reduction factor[10] from stored liquid wastes to bulk stored solids is approximately 10 to 1.

Existing underground storage bins[11] for calcined solids located near the WCF can hold the calcined product from the processing of the contents of about two of these tanks.[8] The off-gas cleanup system[12] has operated very efficiently; radioactivity in the off-gas has been consistently less than one-half of 1% of the established radiation-control guide values (*National Bureau of Standards Handbook 69*). Preliminary information indicates that approximately 95% of the mercury introduced to the fluid-bed calciner is converted to a solid and is transferred with the calcined product to solids storage.[10] Most of the mercury appeared to be retained in the silica-gel adsorbers (for adsorption of ruthenium).

Brown and associates[13] at the ICPP have summarized the results of 12 pilot-plant calciner runs (runs 11 to 22) which were carried out in the 2-ft-square fluid-bed calciner to provide support data for the WCF and to study further the fluidized-bed calcination process. Nonradioactive, simulated aluminum nitrate process wastes were used in these runs. Demonstration of the operability of the feed nozzle selected for use in the WCF and determination of the factors affecting the intraparticle porosity of the calcined (alumina) product were major results of these studies. The sodium concentration of the feed was shown to have a significant effect on the formation of alpha alumina in the product. Neither the presence nor absence of mercury in the feed had any detectable effect on calciner operation or alumina product properties.

An investigation of the various mechanisms by which fines are generated in the fluidized-bed calcination process is being conducted by Grimmett at the ICPP.[14,15] In the fluid-bed calcination of actual plant-level-activity wastes, the fines that are elutriated from the fluid bed and become entrained in the process off-gas are a source of radioactivity which must be removed from the off-gas. An effective method for reducing the amount of fine particles entrained in the off-gas would be to control the rate of generation of elutriatable fines in the fluid bed. Grimmett has proposed a simplified model that depicts the sources of elutriatable fines in the fluidized-bed calcination process. He suggests that these fines are generated by only two mechanisms—spray drying of feed droplets and attrition of bed particles. The model is represented mathematically by two differential equations that can be solved by means of an analog computer. The validity of the model was demonstrated by the good agreement obtained between the computer-determined values and the experimentally determined values from chemical tracer experiments conducted in the 2-ft-square pilot-plant fluid-bed calciner.

Spray Calcination

Work has continued at Hanford on the development of radiant-heat spray calcination for the treatment of Purex-process high-level-activity aqueous wastes.[16,17] In radiant-heat spray calcination, the feed solution is sprayed into the top of a heated column that is maintained at 700 to 750°C. Spray droplets are converted to solids, and some salt decomposition is achieved. The dried residue falls into a melt pot that is used to effect a reduction in volume of the residue. In the melt pot, which is maintained well above the melting temperature (typically 750°C) of the dried residue, further decomposition and melting of the dried residue take place continuously. A spray calciner 10 in. in diameter by 6 ft in height and a melt pot 5 in. in diameter by 13 in. in height were used in these experiments.

In two recent spray-calcination runs,[17] the effect of the use of either sugar or phosphorous acid for suppressing the volatilization of ruthenium from plant-level-activity acidic (2.9*M*) Purex wastes (1WW) was determined. In the run that was made with sugar, sodium bisulfate (0.6 mole/liter of 1WW waste) was first added to produce a meltable calcine. Sugar was then added to reduce the acidity in the 1WW (by decomposing the nitric acid) to a *p*H of 0.1. The ruthenium found in the condensate amounted to about 10% of the original ruthenium present in the 1WW, which may be compared with the 12 to 20% obtained in spray-calcination runs made with plant-level acidic 1WW. [In a run made with low-acid-content (0.2*M*) Redox waste[17] to which glass-forming additives (sodium tetraborate and silica) had been added, the ruthenium in the condensate amounted to 2% of the original ruthenium present in the Redox waste.] The overall decontamination factor for ruthenium in the off-gas after it passed through the absolute filters (final treatment) was about 3×10^7, which represented a ruthenium decontamination factor that was lower than usual but which was still satisfactory for the safe release of the off-gas to the atmosphere.

In the run that was made with phosphorous acid, the acid (0.97*M*) was added to the 1WW to

form orthophosphate compounds with the metal ions present in the waste solution. The ruthenium found in the condensate amounted to only 2% of the original ruthenium present in the 1WW.

Pot Calcination

Oak Ridge National Laboratory (ORNL) is continuing its investigation of the pot-calcination process for converting high-level-activity wastes to solids.[18,19] Laboratory and engineering-scale studies[19–24] are being carried out to provide design information[17] for a pilot plant to be constructed at Hanford.[20] The design of the pot calciner (based on data provided by ORNL) for the pilot plant is being done at Hanford and is about 90% completed.[17] In the pot-calcination process, the plant waste is first evaporated to decrease its volume. The off-gas from the evaporator, which contains essentially all the nitric acid in the original waste, is sent to a fractionation distillation unit to produce concentrated nitric acid for reuse and very dilute nitric acid of a low level of activity. The dilute nitric acid can be further treated for disposal or recycled to the pot-calciner evaporator. The concentrated plant waste from the evaporator is then fed to the calcination vessel for thermal decomposition (at temperatures up to 900°C) of the dissolved solids to metal oxides and sulfates. After the calcination step, the calciner pot of solids is disconnected from the system, sealed, and used as the container for the waste during final storage at a suitable site.

Hancher and associates[19] at ORNL have summarized the results of nine pot-calcination runs in which simulated Purex-plant acid wastes (1WW) were treated with formaldehyde to reduce the nitric acid concentration. The authors have presented detailed data and have evaluated each of the nine pot-calcination tests (R-70 to R-78). The results of six of these runs (R-70 to R-75) have been reported in a previous issue of *Reactor Fuel Processing*.[21] Information regarding the other three runs (R-76, R-77, and R-78) is now given. The composition of the formaldehyde-treated feed material (FTW-65) used in these runs is shown in Table IV-1. The FTW-65 waste is essentially a dilute solution of sodium nitrate containing H^+, Fe^{3+}, Hg^{2+}, SO_4^{2-}, F^-, and PO_4^{3-}.

Table IV-1 COMPOSITION OF SIMULATED FORMALDEHYDE-TREATED PUREX WASTES (FTW-65) FOR ORNL POT-CALCINATION RUNS[19]

Test No.	H^+,* M	g/liter						
		NO_3^-	Fe^{3+}	Na^+	Hg^{2+}	SO_4^{2-}	F^-	PO_4^{3-}
Proposed FTW-65 Purex waste composition (as of 10-1-62)	1.0	82	11	7	1	15	0.1	0.4
R-76†	4.56	346	31	21	1.2	43		
R-77‡	1.14	137	11	27	0.9	60		0.4
R-78‡	6.87	117	6	27	1.7	62		0.4

*H^+ molar by difference.

†Made up three times regular concentration to simulate evaporation before adding glass additives.

‡Threefold excess of sodium as sodium sulfate plus added nitrate.

In run R-76, which was a first attempt at producing a glass in the pot-calciner system, glass-forming additives [NaH_2PO_2, $NaNO_3$, and $Al(NO_3)_3$] were added to the feed solution. The adjusted feed was then fed by gravity to the pot calciner. To reduce sulfate volatility, calcium nitrate (0.17 mole of calcium/mole of sulfate) was added, at a controlled rate, to the pot calciner. However, this run was voluntarily terminated; excessive foaming occurred, and the calciner off-gas line became plugged. The test pot of type 304 stainless steel had corrosion pits about 75 mils deep; the 35-mil-thick cover of type 304 stainless steel on the thermowell was completely corroded. In runs R-77 and R-78, the feed material contained four times the typical sodium sulfate content in order to simulate a high-sodium-content waste to which sulfate had been added to reduce sodium volatilization. Calcium nitrate was also added to the pot calciner in these tests to reduce sulfate volatiliza-

Table IV-2 COMPOSITION OF CALCINED SOLIDS FOR FTW-65 PUREX POT-CALCINATION TESTS[19]

Test No.	Total feed volume, liters	Calcining time, hr	Bulk density, g/cm³	NO_3, ppm	Fe, wt.%	Na, wt.%	Hg, wt.%	SO_4, wt.%
R-76	188		2.8*					
R-77	726	25	1.26	100	8.85	23.6	3.04	55.7
R-78	904	31	1.36	100	3.55	28.0	3.08	59.6

*Density measured by displacement.

tion. The operation of the pot calciner with this type of feed was fairly difficult because of the foaming tendency of the feed. The foaming resulted in more entrainment in the off-gas line than in runs made with FTW-65 of the usual composition (see Table IV-1). The composition of the calcined solids for the two tests is shown in Table IV-2. The higher density for the calcined solid obtained in run R-78 was primarily the result of a higher volume of feed being processed. The calcium (as calcium nitrate) that was added to combine with the sulfate was 10% of the total sulfate present. Of the total amount of sulfate fed to the system, less sulfate was found in the calciner pot condensate in run R-77 (0.07%) than in run R-78 (25%). The higher amount in run R-78 was due to the large amount of carry-over in the calciner off-gas line. However, this type of feed can probably be handled satisfactorily with the addition of a larger deentraining section to the pot calciner. In these two tests, very little corrosion occurred; the two feed streams contained no fluoride, and a controlled addition of calcium was used throughout. The decontamination factors for the evaporator and the pot calciner, and the overall decontamination factor for the process system, are shown in Table IV-3.

Rotary-Ball Kiln Calcination

A calcination process (see Fig. IV-7) that utilizes a rotary-ball kiln calciner is being developed at Brookhaven National Laboratory (BNL) for the treatment of high-level-activity high-salt-content aqueous wastes.[1,23–27] This method of calcination was undertaken at BNL because it appeared to offer the following advantages: continuous operation, dust control through condensation of off-gases, efficient heat input, and uniformity of product. This work is being carried out with nonradioactive, simulated waste feed materials in a pilot plant (see Fig. IV-8) at BNL. The process and operating information obtained will be used for the design of a rotary-calciner demonstration plant for studies with plant-level-activity wastes.[1] The calciner, which is fabricated of Inconel X, is 8 in. in diameter by 7 ft in length.[1,24] It is externally heated along its length by means of a resistance

Table IV-3 DECONTAMINATION FACTORS FOR ORNL POT-CALCINATION RUNS R-77 AND R-78 (Ref. 19)

	Run R-77			Run R-78		
	Evaporator*	Pot calciner†	Overall‡	Evaporator*	Pot calciner†	Overall‡
Iron	18,820	400	7,260	32,500	3	5,420
Sodium	42,920	790	9,910	11,100	5	24,590
Mercury	115	19.5	20.4	650	2.3	34.8
Nitrate	5.4	1.0	1.3	5.0	1.0	0.7
Sulfate	13,120	1,410	1,380	4,960	5	1,840

*The decontamination factor for the evaporator is the average concentration in the evaporator concentrate divided by the average concentration in the evaporator condensate.

†The decontamination factor for the pot calciner is the total amount of the component fed to the calciner divided by the total amount of the component in the calciner condensate.

‡The overall decontamination factor is the total amount of the component fed to the system divided by the total amount of the component in the evaporator condensate.

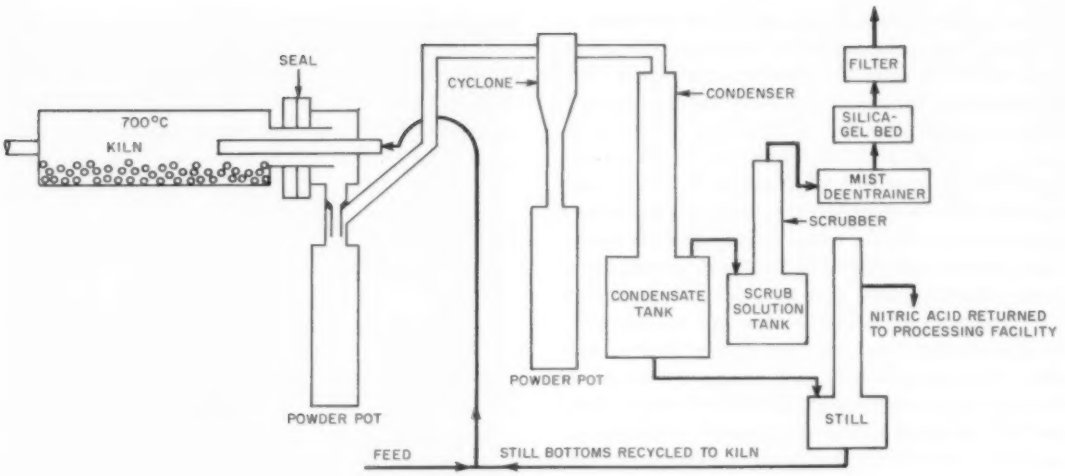

Fig. IV-7 BNL rotary-calciner flow sheet.[1]

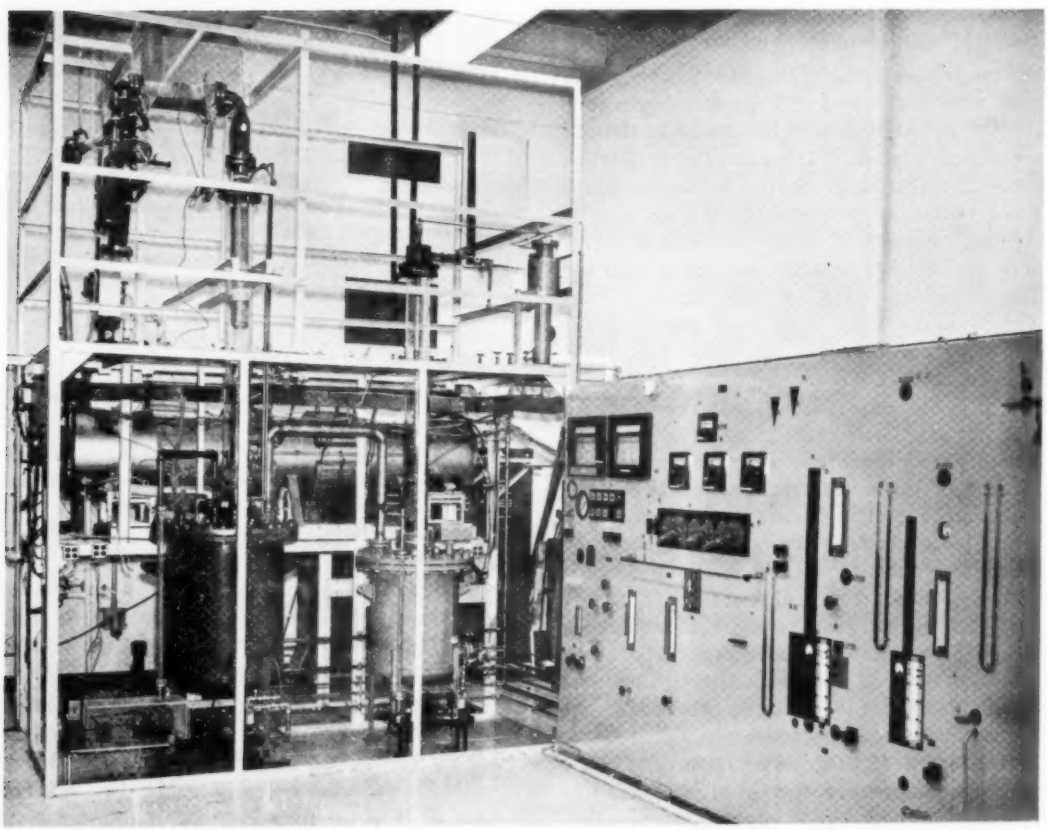

Fig. IV-8 Rotary-calciner pilot plant at Brookhaven National Laboratory.[21] (Courtesy of Brookhaven National Laboratory.)

furnace. The calciner is rotated at a rate of 1 to 5 rpm and is operated at a design temperature of 700°C. The feed that is introduced into the calciner by means of a pressure-cycled feed spray system[26,27] (5 gal/hr) falls on a shallow bed of stainless-steel balls (¾ in. in diameter). The metal balls serve to aid in heat transfer and to prevent the formation of large agglomerates during calcination. The calcined oxide product overflows from the discharge end of the calciner into a heated powder receiver. (The rotating calciner is attached to the stationary powder receiver by means of a rotary seal.) The off-gases from the calciner pass out the discharge end of the calciner where they are then handled in the off-gas cleaning system (see Fig. IV-7). Since no noncondensable gases are added to the system, direct condensation of the off-gases offers an excellent means for control of calcine particles that are carried over from the calciner. The small portion of noncondensable gases present is treated by being passed through a scrubber and absolute filter.

The main development program has been concerned with the design of a satisfactory rotary seal[1,24–27] rather than with the design of the off-gas cleaning system.[24] The rotary seal must be capable of operating at an elevated temperature and in a radiation environment.[1] It must also be protected, because of the presence of abrasive dust in the calciner, against excessive wear and galling of moving parts. Of three different types of rotary seals which have been tested in the pilot plant, a rotary gap seal (see Fig. IV-9) developed at BNL has proved to be most satisfactory.[26] The seal design features a small (0.002 in.) gap between the faces of the rotating and nonrotating disks, the gap being maintained by means of three rollers mounted at the periphery, and a continuous inward flow of superheated steam through the gap to oppose any tendency for outward escape of gases or dust from the calciner. The seal was tested in an extended, continuous run of some 800 hr in which 2500 gal of simulated aluminum nitrate (1.6*M*) waste solution was calcined. Although the seal was found to have a high degree of leaktightness and showed satisfactory operation with a steam consumption of 40 lb/hr at a pressure of 2 to 3 psig in the seal groove, the need for further improvement in the design of the seal became evident when excessive wear and galling were found along the line of contact between the rollers and supporting face of the stationary disk. (The rollers and the stationary disk were both made of stainless steel.) It is believed that the use of a hardened metal in the fabrication of the stationary disk and, possibly, of the rollers would eliminate this defect in the mechanical design of the unit.

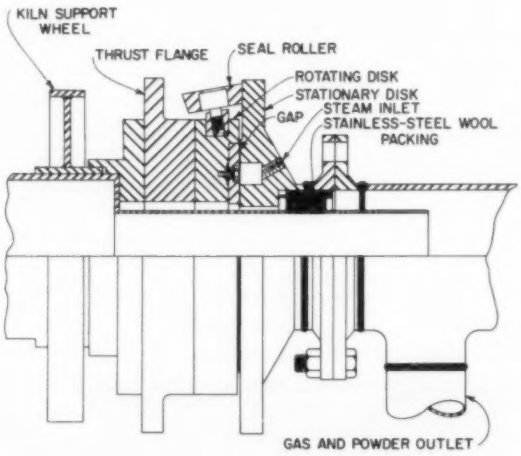

Fig. IV-9 Rotary gap seal for BNL rotary calciner.[26]

Operation of the pilot plant during this run was considered satisfactory in most respects. Only minor difficulty, due to cake formation in the calciner, was experienced.

Conversion to Glasses

Studies[25–28] are continuing at BNL on the development of a continuous process for the conversion of high-level-activity wastes to stable phosphate glasses.[1] In this process the entire conversion of the raw aqueous waste to the final glass product is carried out in an all-liquid system. A number of preliminary runs with nonradioactive, simulated Purex wastes have been satisfactorily completed in the BNL pilot plant[27] (see Fig. IV-10). Rates of phosphate glass production up to 1.9 cu ft/24 hr have been achieved. (It is estimated that 1 cu ft of phosphate glass would be produced in the treatment of high-level-activity waste from the processing of fuel containing 1 ton of uranium.)

A platinum crucible (8 in. in diameter by 12 in. in length) is being tested in the pilot plant to evaluate platinum as a suitable corrosion-resistant material for containing molten Purex

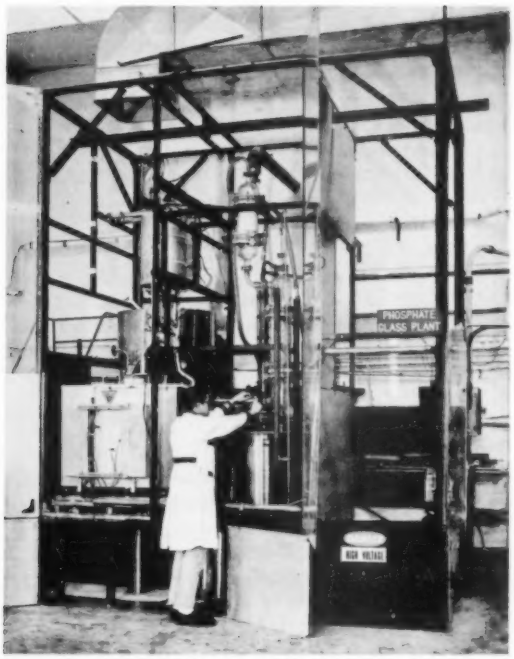

Fig. IV-10 Phosphate glass pilot plant at Brookhaven National Laboratory.[27] (Courtesy of Brookhaven National Laboratory.)

phosphate glass at 1200°C (Refs. 26 to 28). For the 5000 hr during which the platinum was exposed to the molten Purex phosphate glass, no signs of deterioration that could be attributed to corrosion were observed.[27]

A demonstration of the BNL continuous phosphate glass process is to be conducted at Hanford in the High-Level Radiochemistry Facility.[17] The process flow sheet will be tested with plant-level-activity Purex acid wastes (1WW) in a small-scale apparatus. Designs for the apparatus are being developed by Hanford and BNL.

Harwell Process for Fixation of Radioactive Wastes in Glass

Elliot and associates[1] at Harwell have described a process for incorporating high-level-activity wastes in glass. A general flow sheet of the process is shown in Fig. IV-11. In the process the wastes are converted to a leach-resistant glass, incorporating up to 35% waste oxides. The conversion is conducted in stainless-steel cylinders that also serve as long-term storage containers. Three cylinders, each 6 in. in diameter by 5 ft in length, are used in series. The first cylinder is the process vessel, which is in a segmented furnace to regulate the heat input along the cylinder's length and is held at 1050°C; the other two cylinders, which are the primary and secondary filter vessels, respectively, are in ovens that are held at 250°C to prevent condensation. The waste solution is first mixed with silica and borax in the correct proportions to produce the required glass composition, and the mixture is then fed to the first cylinder for conversion of the waste to a glass. The process cycle is stopped when the cylinder is filled with about $3\frac{1}{2}$ ft of glass. The off-gases from the process vessel pass first through the other two cylinders, each containing a filter (packed with ferric oxide for adsorption of volatile ruthenium), then to a condenser and adsorber (for oxides of nitrogen), and ultimately to a caustic scrubber system before being passed through a final absolute filter. After the process cylinder containing the glass is removed from the furnace to storage, the second cylinder (containing the spent primary filter) is placed in the furnace. As the furnace temperature is raised at the beginning of the next process cycle, a zinc weld connecting the spent primary filter to the cover melts (420°C), and the filter drops to the bottom of the cylinder. A new cylinder (with primary filter) is then installed in the first oven. The third cylinder, because it contains a high-capacity filter (and adsorber), is not expected to be moved through the process cycle. During the processing cycle the pressure in the equipment is maintained below atmospheric pressure.

The process has been demonstrated successfully in pilot-plant runs in which 50-kg blocks of leach-resistant glass have been formed from low-level-activity simulated waste solutions. A pilot plant has been constructed to produce glass blocks containing up to 1000 curies of fission-product activity.

Laboratory investigations at Harwell have shown that the borosilicate glass system used in this process is a very satisfactory medium for long-term storage of high-level-activity wastes.[1] The glass formed is almost insoluble in water; devitrification of the glass or high radiation doses do not significantly affect its solubility. Also, the borosilicate glass does not corrosively react, even at the temperature of its manufacture (1050°C), with the stainless-steel process vessel.

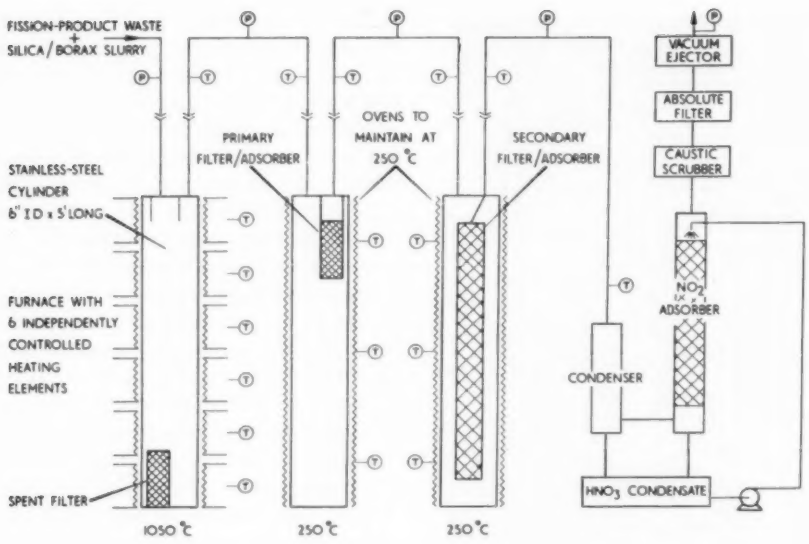

Fig. IV-11 Simplified flow sheet of Harwell process for incorporation of fission-product wastes into glass.[1]

Glass Fixation Process Studies in France

Bonniaud and Rançon[1,28] at the Centre d'Étude Nucléaires, Fontenay-aux-Roses, France, have described three vitrification processing techniques being investigated in France for the treatment of high-level-activity wastes. (Currently these wastes are concentrated in evaporators prior to storage in tanks. It is this evaporator concentrate which is to be further processed by a fixation procedure.)

Batch, continuous, and semicontinuous processes are being studied. The batch process is carried out in crucibles and consists of the following steps: (1) adding a gelling agent and glass frit to the concentrated waste, (2) pouring the mixture, while it is still fluid, into a crucible, and (3) after gelling occurs, evaporating and melting the resultant hard compact mass. An installation to demonstrate this process is being constructed. It is being designed to produce glass blocks containing up to 10,000 curies of fission-product activity.

The continuous process comprises a rotary calciner that is coupled to a continuous melting furnace where the glass-forming additives are charged. After melting, the glass is run out through an overflow point at the base of the furnace. An installation capable of handling 100 liters of waste solution per day has been constructed to test this process. The results of runs conducted in this installation have shown that further work must be done to reduce entrainment of fines in the off-gas from the calciner and to reduce volatilization of ruthenium. Modifications have been carried out on the calciner which would reduce the amount of air inleakage to the calciner.

The semicontinuous process involves the use of metal pots in which simultaneous evaporation and calcination of the waste solution (to which a gelling agent and glass frit have been previously added) are initially carried out, followed by fusion of the calcined material at a higher temperature. While the glass is still fluid, it is run out of the pot (through a tapping tube in the bottom of the pot) to a storage receiver. Thus the pot can be recycled for further use. An installation to demonstrate this process is being built. It will utilize an induction-heated Inconel pot, 20 cm in diameter by 2 m in height.

Conversion to silicate type glasses[1,30] has been found suitable for the high-level-activity wastes produced from the processing of irradiated, natural-uranium fuel at the Marcoule (France) plutonium extraction plant. These wastes have been previously concentrated by means of evaporators prior to tank storage as liquids. (Phillip Fineman)

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Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, and Plutonium and Their Compounds

Production of Uranium Dioxide

Reduction of Uranium Trioxide

Gas-solid reactions, particularly the reduction of uranium trioxide with hydrogen and the hydrofluorination of uranium dioxide to produce uranium tetrafluoride, are important steps in the production of both uranium metal and uranium hexafluoride. The rate of these reactions has been shown to be determined by the structure of the solid surface which, in turn, is modified by the progress of the reactions. Vlasov and Zhukovskii have studied the kinetics of the reduction of uranium trioxide by nitrogen-hydrogen mixtures[1] at temperatures of 350 to 500°C and by undissociated ammonia[2] in the temperature range 300 to 450°C. The uranium trioxide used in both studies was an amorphous material with a specific surface area of 15 m^2/g. The material was prepared by heating $UO_4 \cdot n H_2O$ in oxygen at 350°C for 4 hr with a subsequent heating at 400°C for 1 hr. The nitrogen-hydrogen gas mixture ($3H_2 + N_2$) was prepared by passing gaseous ammonia through a nickel catalyst bed at 930°C.

It was observed[1] that the reduction of uranium trioxide to uranium dioxide by nitrogen-hydrogen mixtures can be separated into four stages: $UO_3 \xrightarrow{1} UO_{2.92} \xrightarrow{2} UO_{2.55} \xrightarrow{3} UO_{2.25} \xrightarrow{4} UO_2$. The rate of reduction of UO_3 is constant at the outset and remains so until the overall composition of the solid phase corresponds to $UO_{2.92}$. The rate then increases, passes through a maximum, and then decreases until $UO_{2.55}$ is reached. A constant rate of reduction is observed in the interval $UO_{2.55} \rightarrow UO_{2.25}$. The final stage of the process is one in which the rate continually diminishes as the reduction progresses. Apparent activation energies calculated for each interval of the reaction were between 26.5 and 31.7 kcal/mole.

The reduction of uranium trioxide by ammonia[2] is said to proceed by the following mechanism: adsorption of gaseous ammonia on the oxide surface, decomposition of the adsorbed ammonia into atomic nitrogen and hydrogen, chemical reduction involving a change in the valence of uranium from 6 to 4 and the removal of oxygen from the oxide lattice, rearrangement of the crystal lattice of the oxide phase, desorption of molecular nitrogen from the oxide surface, and desorption of water from the oxide surface. The apparent activation energy of the reduction is 45.3 kcal/mole, which suggests that the reduction reaction is limited chiefly by the desorption of nitrogen from the oxide surface. In the reduction of UO_3 by nitrogen-hydrogen mixtures, the limiting step was the interaction between the hydrogen and the oxide oxygen in the adsorbed layer.[1] Comparison of the two reduction processes has shown[1] that UO_3 is more readily and completely reduced by N_2-H_2 mixtures than by NH_3. At 450°C the reduction by N_2-$3H_2$ goes to $UO_{2.08}$, whereas with NH_3 the reduction ceases with the formation of U_3O_8. The rate of reduction with $3H_2$-N_2 mixtures increases linearly with an increase in hydrogen pressure. With ammonia the reduction reaction is retarded by an increase in ammonia partial pressure.

Conversion of Uranium Hexafluoride to Uranium Dioxide

High-density spheroidal uranium particles, suitable for application in dispersion or vibratory-compacted or swaged fuel elements, have been prepared at Argonne National Laboratory (ANL) directly from uranium hexafluoride in a continuous single-step operation employing fluidization techniques.[3–5] Uranium

hexafluoride is fed continuously into a fluidized bed of uranium dioxide particles and reacted at 650 to 700°C with a mixture of steam and hydrogen. Development studies are being made in a 3-in.-diameter Monel column to define the processing conditions that result in the production of dense UO_2 particles. The results of previous studies reported in *Reactor Fuel Processing*[6] indicated that UO_2 particles with a density of 9.8 g/cm^3 can be prepared under certain prescribed processing conditions. Recent studies[3] have shown that the height of the fluidized bed of UO_2 particles has little effect on the density of the uranium dioxide product. In a test employing an 11-kg bed of UO_2 (equivalent to an 18-in. static bed height), particles with a density of 9.6 g/cm^3 were produced, and this density is similar to that obtained previously[6] in tests with 8-in.-deep beds. High-density particles have been obtained[3] with a hydrogen excess of four times the stoichiometric requirement (based on the reaction $UF_6 + H_2 + 2H_2O \rightarrow UO_2 + 6HF$). It was observed in tests with low hydrogen excess that the residual fluoride content in the UO_2 (650 ppm fluoride) was significantly greater than in tests employing hydrogen excess of 10 to 20 times stoichiometric (380 ppm fluoride).

Several tests were performed to demonstrate the feasibility of preparing dense UO_2 particles of specific size fraction which might be suitable for particulate nuclear fuels.[4] Dense oxide, primarily in the 80- to 100-mesh range, was produced from a starting bed of 100- to 140-mesh UO_2 particles. The preparation of relatively coarse (+20 mesh) particles from a starting bed of 20- to 40-mesh UO_2 by this procedure does not appear feasible since only slight particle growth occurred and many fragmented sections of coating were found in the product.

Sintering Properties of Uranium Dioxide

Most water-cooled water-moderated nuclear power reactors utilize sintered uranium dioxide as the fuel. This fuel must be of high density (>93% of theoretical density) to assure dimensional stability of the fuel and a high degree of fission-gas retention. The development of economic processes for the production of sintered UO_2 of high density is of fundamental importance in reactor fuel concepts. Uranium dioxide powders are produced by several different methods, and the properties of the powders are greatly affected by the preparation method. Doi and Ito[7] have examined in detail the effect of ammonium diuranate (ADU) precipitation conditions on the characteristics and sintering behavior of uranium dioxide. Ammonium diuranate is converted to UO_3 by calcination in air for 3 hr at 400°C. Uranium trioxide is reduced to UO_2 by reaction with hydrogen. The important powder properties necessary for high degree of sinterability have been defined as (1) fine average particle size; (2) moderately high reactivity of the powder; and (3) loose, homogeneous agglomeration of elementary particles. Experimental results revealed that the structural features of the ADU precipitate affects remarkably the progress of free sintering of the UO_2. Calcination of the ADU precipitate at temperatures as low as 400°C does not appreciably modify the physical state of the precipitate. Since firing of the UO_3 in hydrogen at temperatures lower than 900°C does not result in extensive sintering of the UO_2 product, it follows that the main features of the ADU precipitate persist throughout calcination and reduction when these operations are performed at comparatively low temperatures. Calcination of ADU at 600°C extensively modifies the physical state of the precipitate by enhanced bridge formation between elementary particles and accelerated growth of U_3O_8 particles. These physical modifications exhibit a marked effect on the sintering behavior of the UO_2 product.

Lowering of the uranium concentration in the initial uranyl nitrate solution prior to ADU precipitation leads to the formation of small elementary ADU platelets and a more homogeneous agglomerate. This results in improved homogeneity in the microstructure of the UO_2 particles at the early stages of sintering. The sintering proceeds to the formation of dense, coarse UO_2 particles. This homogeneity in microstructure of UO_2, resulting from natural agglomeration in the ADU precipitate, gives rise to even more rapid grain growth and sintering than is achieved by cold compaction of UO_2 powders.

The effects of a steam atmosphere on the sintering of uranium dioxide powders have been observed by Baily and associates at Westinghouse.[8] Uranium dioxide pellets of considerably higher densities were attained by sintering in a steam atmosphere at 1200 to 1400°C than in a hydrogen atmosphere in the same temperature

range. It was observed that sintering of UO_2 in steam begins at temperatures as low as 750°C, whereas much higher temperatures are required for sintering in hydrogen. During steam sintering a nonstoichiometric single-phase structure UO_{2+x} is formed at elevated temperatures with oxygen-to-uranium ratios as high as 2.23. Upon cooling, the equilibrium low-temperature phase U_4O_9 precipitates out in the UO_2 matrix. The oxygen-to-uranium ratio may be readily reduced to 2.01 by cooling the UO_2 compacts in a hydrogen atmosphere after steam sintering.

A process for producing small sintered UO_2 spheres of high density based on isostatic pressing has been described by Bondesan and associates.[9] The UO_2 feed material is ground and blended with an aqueous solution of a binder to form a paste, which is then dried to 25 wt.% water. This material is extruded to form a small-diameter rod that is cut into right cylinders. The cylinders are then formed into small spheres, dried at 25°C to 3 wt.% water, and finally pressed in a cylindrical die under a pressure of 2 tons/cm^2 for 10 min. The pressed spheres have a density of 6.2 g/cm^3. The spheres are sintered in a hydrogen atmosphere at 1650°C to a density of 10.65 g/cm^3.

Workers in France have developed a process for producing sintered UO_2 shapes on a continuous basis.[10,11] A series of tests performed to evaluate granulation procedures resulted in the conclusion that procedures based on wet methods are inferior, and a method based on dry granulation without a binder was adopted.[10] Definite advantages were obtained by the use of a continuous sintering furnace rather than a batch furnace. Sintered UO_2 bodies with densities greater than 10.5 g/cm^3 were obtained by firing for 6 hr in cracked ammonia at 1650°C. Considerable regularity of characteristics of the sintered products was observed in tests at a production rate of 4 tons/month.[11]

Uranium dioxide has a marked tendency to oxidize in oxygen, which is apparent even at room temperature, especially when the UO_2 is in a divided state. A study has been made by Brandela and Delmas[12] to determine the conditions under which UO_2 is oxidized in H_2-O_2 gas environments, with direct application to the production of sintered UO_2 bodies. It was observed that hydrogen containing 0.5 vol.% O_2 is a reducing agent at temperatures above 420°C and an oxidizing agent below 420°C. The oxidation rate in this gas mixture is a maximum at 260°C.

Oxidation of sintered UO_2 may be expected to occur during the cooling period following sintering if the gas phase is not completely free from oxygen. Superficial oxidation of sintered UO_2 has been observed to occur *in vacuo* at 400°C with an oxygen pressure of 2.5×10^{-5} atm and at 650°C with 0.5×10^{-5} atm oxygen pressure.[12]

Two articles have been published recently which review nonstoichiometry in the uranium oxide system.[13,14] Lynds and associates[13] have made a thorough investigation into the UO_2-U_4O_9 composition range. In an article devoted to fluorite type oxides, Roberts[14] discusses the thermodynamic properties of nonstoichiometric uranium oxides.

Production of Uranium Carbides

Interest in using the carbides of uranium as nuclear fuels has grown considerably within the past few years and has stimulated research and development work in many countries. This recent interest in uranium carbides has generated a large volume of published information on the physical properties of the carbides and descriptions of methods of producing and fabricating carbide bodies. Frost[15] has reviewed the present state of knowledge of the physical properties of uranium carbides with particular emphasis placed on uranium monocarbide. Summaries of papers presented at the Fourth Uranium Carbide Conference have been published recently.[16] Representatives from 13 organizations doing development work on uranium carbide in the United States participated. In addition, several representatives from Germany, England, and France presented papers relating to development work carried out in their establishments.

Sintering of Uranium Monocarbide

In the fabrication of uranium carbide bodies for use as a nuclear fuel, it is essential that densities 95% of theoretical be achieved. Taylor, McMurtry, and Andersen[16a] have observed that the use of small amounts of nickel as a sintering aid was successful in obtaining high-density pellets of uranium monocarbide. The

Table V-1 EFFECT OF NICKEL ON THE DENSITY OF SINTERED UC[16a]

(Time at Temperature, 4 Hr)

Nickel, wt.%	Bulk density (g/cm³) when sintered at:			
	1485°C	1525°C	1600°C	1800°C
None	9.15	9.28	11.45	12.35
1.0	12.75	12.85	*	*
0.5	12.95	12.98	*	*
0.1	11.40	12.98	12.75	12.60
0.05	10.60	12.55	12.15	12.37
0.025	10.20	10.50	11.92	12.27

*Pellets reacted with tantalum setter.

addition of 0.1 to 0.2 wt.% nickel made it possible to obtain densities 95% of theoretical while lowering the sintering temperature 400°C. The effect of nickel on the density of sintered UC is shown in Table V-1. The optimum amount of nickel appears to be in the range 0.1 to 0.5 wt.%, and the optimum sintering temperature is approximately 1525°C.

The use of nickel as a sintering aid in the fabrication of uranium monocarbide compacts promotes the formation of a second phase that appears to be uranium sesquicarbide (U_2C_3). Annealing the monocarbide compacts at 1850°C, which is above the stability range of U_2C_3, results in the disappearance of the sesquicarbide phase and the formation of minor amounts of UC_2. Further annealing at 2150°C causes the dicarbide to disappear, and uranium metal is formed at the grain boundaries. The presence of 5% UC_2, 5% UO_2, and 10% UN showed no effect on the final density of sintered UC compacts containing 0.15% nickel (Table V-2).

The use of nickel as a sintering aid has been extended to the preparation of high-density UC-PuC compositions.[16a,16b] Microprobe analyses of samples of $(U_{0.8}Pu_{0.2})C_{0.95}$ and $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1 wt.% nickel showed that both the plutonium and nickel are uniformly distributed throughout the material and that nickel is not concentrated at grain boundaries.[16b]

Hammond and associates[16c] at Oak Ridge National Laboratory (ORNL) have developed a method for the fabrication of uranium monocarbide with UAl_2 as a sintering aid. By sintering UC with 5 to 10 wt.% UAl_2 in a vacuum of 10^{-6} to 10^{-7} torr at 1350 to 1400°C, they obtained single-phase uranium monocarbide bodies with densities in excess of 97% of theoretical. As a result of the high vapor pressure of aluminum, this element is removed through the vacuum manifold of the furnace during sintering. The uranium introduced with the UAl_2 sintering aid is combined with carbon introduced as an excess in the UC feed material.

Synthesis of Uranium Monocarbide from U_3O_8

Lovell[17] has described a method for synthesizing uranium monocarbide by the carbon reduction of U_3O_8. The reaction proceeds in two steps, with the formation of UO_2 as an intermediate compound. In the first step the reduction of U_3O_8 to UO_2 with carbon takes place according to the equation $U_3O_8 + C \rightarrow 3UO_2 + CO_2$. This stage of the reaction is carried out by heating U_3O_8 and carbon in vacuum at about 620°C. To assure an adequate rate of reaction, the temperature of the system is gradually increased to 700°C and maintained at that value until the reaction is complete. Reduction to UC is carried out in the second step by heating the UO_2-carbon mixture in vacuum at temperatures between 1220 and 1450°C. Sintering of the UC product is accomplished by heating at 1700°C for 3 hr. Uranium dicarbide has also been prepared directly from U_3O_8.

Coating of Uranium Carbides

The encapsulation of individual nuclear fuel particles with ceramic coatings is being investigated primarily to prepare fuel materials for use in gas-cooled reactors. In the case of carbide fuels, both the fuel and fertile material

Table V-2 DENSITY OF SINTERED UC AND OF SINTERED UC CONTAINING 0.15 WT.% NICKEL PLUS OTHER ADDITIVES[16a]

Composition	UC	UC + Ni	UC + Ni +5% UO_2	UC + Ni +5% UC_2	UC + Ni +10% UN	UC + Ni +10% U
Sintering temp., °C	1940	1525	1525	1525	1525	1525
Density, g/cm³	12.5	13.1	13.1	13.2	13.1	13.3
Phases identified by metallography	U (trace)	U_2C_3	U_2C_3 and UO_2	U_2C_3	U_2C_3	U

for the Peach Bottom and Dragon reactors are in the form of ceramic-coated carbide particles uniformly dispersed in a portion of the graphite moderator. Dayton, Oxley, and Townley[18] have recently reviewed the technology of preparing ceramic-coated nuclear fuel particles and the results of performance tests in radiation and high-temperature environments. In another review article, Oxley[19] presents the recent developments in coated-particle fuel materials. It should be mentioned that information concerning coated-particle fuels is periodically reviewed in *Reactor Materials*.[20–22] These reviews particularly emphasize the evaluation of coated-particle fuels in performance tests. A symposium devoted to coated-particle fuels was included in the November 1963 national meeting of the American Nuclear Society. Summaries of the nine papers presented at the symposium were published in the transactions of the Society.[23]

Plutonium Compounds

Preparation of Plutonium Dioxide

The standard feed for the production of plutonium metal or compounds is a dilute solution of plutonium in nitric acid from the Purex solvent-extraction process. Recovery of plutonium from the nitrate solution is effected by precipitation of Pu(IV) oxalate or peroxide. These materials are readily converted to plutonium dioxide by calcination at 600°C. Ganivet[24] has studied the Pu(IV)-oxalate system to determine the conditions necessary for complete precipitation of plutonium oxalate. From a determination of the dissociation constants of the plutonium oxalate complexes, Ganivet[24] derived a mathematical expression relating the solubility of $Pu(C_2O_4)_2$ to the *p*H of the solution. The recommended optimum conditions for oxalate precipitation involve the use of a Pu(IV) nitrate solution free from Pu(VI) ions and with an acidity near 1*N*. The quantity of oxalic acid added to the nitrate solution must provide an oxalate-ion concentration in the supernatant solution between $2 \times 10^{-2}M$ and $5 \times 10^{-2}M$. Under these precipitation conditions the solubility of plutonium oxalate is approximately 25 mg of plutonium per liter.

Workers at Société Belge pour l'Industrie Nucléaire and Centre d'Étude de l'Énergie Nucléaire have studied the precipitation of several plutonium salts from nitric acid solutions.[25,26] The objective of the study was to determine which plutonium salt upon calcination produces plutonium dioxide of high density. Comparisons of PuO_2 produced from plutonium oxalate, plutonium hydroxide, and plutonium peroxide were made on the basis of the ease of sintering of the oxide to high-density pellets. It was observed[25] that PuO_2 prepared from plutonium oxalate and plutonium peroxide possessed a high surface area and sintered rapidly, resulting in the formation of voids within the pellets and thus producing a low-density compact. Oxide produced from plutonium hydroxide appeared most suitable for the preparation of high-density shapes. Plutonium hydroxide is precipitated by the addition of ammonium hydroxide to the plutonium nitrate solution.[26] The precipitate begins to form at a *p*H of 3.5 and is complete at a *p*H of 6.5. The solubility of Pu(IV) hydroxide at 30°C with a *p*H of 6.5 is 0.3 mg of plutonium per liter. Filtration of the solution is slow but becomes much more rapid if the precipitation is carried out at higher temperatures. Plutonium(IV) may also be precipitated as the hydroxide through the hydrolysis of urea at 95°C. The filtration characteristics of the precipitate are excellent. It was observed[26] that the oxide obtained from plutonium hydroxide precipitated from hot solutions is entirely unsuitable for pellet manufacture because of the low bulk density of the oxide. High-density plutonium dioxide pellets (10.7 g/cm^3) have been prepared from plutonium hydroxide precipitated at room temperature by calcining the hydroxide in air at a temperature of 400°C, followed by sintering in an atmosphere of moist hydrogen at 1300 to 1600°C.

Jenkins and Waterman[27] have studied the thermal decomposition of hydrated Pu(IV) oxalates in air and in nitrogen over the temperature range 20 to 830°C. In air the oxalates begin to lose water of hydration at 45 to 60°C, and, in the temperature range 200 to 290°C, a mixture of PuO_2 and $Pu(CO_3)_2$ is formed. No evidence was found for the formation of any stable intermediate hydrate, or anhydrous Pu(IV) oxalate, or Pu(III) oxalate. An intermediate compound corresponding to $Pu(CO_3)_2$ was observed in the decomposition of plutonium oxalate in nitrogen.

A process for the preparation of metallic plutonium using a chloride intermediate is being developed at Hanford Atomic Products Operation (HAPO).[28,29] The proposed process includes

calcination of plutonium nitrate to PuO_2, chlorination of PuO_2 to $PuCl_3$, and electrolytic reduction of $PuCl_3$ to metallic plutonium. Calcination of plutonium nitrate to plutonium dioxide is carried out in a continuous trough type calciner[30] at temperatures of 230 to 275°C. The calciner is constructed of stainless steel and is 12 in. in length, 3 in. in diameter, and 3 in. in height (Fig. V-1). The plutonium oxide bed is agitated by means of a nonconveying scraper blade located concentrically within the trough. It was observed[30,31] that plutonium dioxide produced by direct calcination of plutonium nitrate solution tended to be relatively unreactive toward chlorination to form $PuCl_3$ as compared with oxide produced by calcination of plutonium oxalate. A series of preliminary tests has been made to establish those factors which affect the reactivity of plutonium dioxide toward chlorination by phosgene.[30,31] Those factors which resulted in PuO_2 of highest reactivity were small particle size, short residence time in the calciner, temperature of calcination between 230 and 275°C, and the presence of a sulfate or oxalate additive in the plutonium nitrate feed solution. The addition of 0.5 mole of ammonium sulfate per mole of plutonium to the nitrate feed solution is effective in producing PuO_2 with an open crystal structure. The sulfate is completely removed during chlorination.

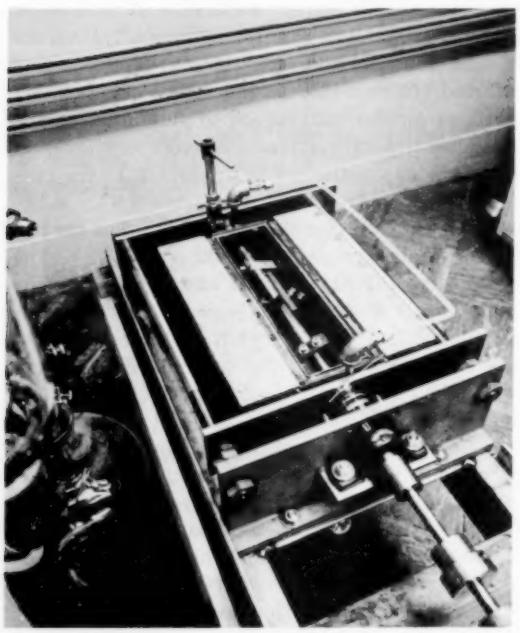

Fig. V-1 Plutonium nitrate calciner[30] with lid removed.

Chlorination of plutonium dioxide with phosgene is carried out at 500°C. An activation energy of 17.2 kcal/mole has been calculated[31] for the reaction. Rasmussen and associates[30] have considered the use of a fluid-bed reactor for the conversion of PuO_2 to $PuCl_3$. The reasons for the choice of a fluid-bed reactor over a vibrating-tube reactor (described previously in *Reactor Fuel Processing*[29]) are better temperature control and the larger holdup time, which would allow complete chlorination of less reactive powder.

Preparation of Plutonium Carbide

In an investigation of the reactions between plutonium dioxide and carbon, Skavdahl[32] has reported the existence of a stable plutonium monooxycarbide phase. The reaction sequence, depending on the amount of carbon added, was determined to be:

$$PuO_2 \xrightarrow{C} \alpha\text{-}Pu_2O_3 \xrightarrow{C} \beta\text{-}Pu_2O_3 \xrightarrow{C} \begin{matrix} [Pu(O,C) + \beta\text{-}Pu_2O_3] \rightarrow PuO \\ \uparrow \\ [Pu_2C_3 + \beta\text{-}Pu_2O_3] \\ \downarrow \\ [Pu(O,C) + Pu_2C_3] \rightarrow PuC \end{matrix}$$

Pressed pellets of mixtures of PuO_2 and carbon powders were reacted at temperatures ranging from 1200 to 1850°C in either vacuum or a flowing helium atmosphere. It was observed that an initial reaction started at about 1300°C and was followed by the release of large volumes of gas (CO) at 1400 and 1625°C. The monooxycarbide [Pu(O,C)] phase is considered to be essentially a solid solution of the isomorphous compounds PuC and PuO.

Johnston, Lonadier, and Powers have prepared a bibliography[33] on the preparation and properties of plutonium carbide. Kruger[34] has described the preparation of plutonium-carbon alloys in the composition range 42 to 60 at.% carbon by arc-melting and drop-casting techniques.

Production of Plutonium Metal

Continuous electrowinning of plutonium metal from plutonium trichloride has been successfully

demonstrated in nuclearly safe equipment at Hanford.[35] Nuclear safety is achieved by restricting the system in a 57-mm-diameter envelope. The cell was designed to operate with the continuous removal of molten plutonium metal through an overflow weir located in the bottom of the refining cell (see Ref. 36, Fig. III-8). The electrolyte system consisted of 30 wt.% $PuCl_3$, 28 wt.% $BaCl_2$, and 42 wt.% KCl. The cell anode was a graphite semicylinder, and molten plutonium served as the cathode. The electrolyte and molten metal were contained in a $MgO-10\%\ TiO_2$ ceramic cylinder. Dry hydrogen was introduced above the molten salt to react with the anode product gases, thus reducing corrosion in the cell off-gas system.

The cell has been successfully operated in a continuous manner with a $PuCl_3$ feed rate of 70 g/hr. In tests performed at 800°C with a cell current of 30 amp, an average current efficiency of 60% was attained with nominal current densities of 2 amp/cm^2 at the anode and 3.2 amp/cm^2 at the cathode. The system has demonstrated the capacity for handling $PuCl_3$ feed containing up to 20 wt.% PuO_2 and for removing feed impurities that form low-boiling chlorides.

Fused-salt electrorefining processes have been developed at Los Alamos Scientific Laboratory (LASL) for producing high-purity high-density plutonium metal on the 500-g and 3.5-kg scale.[37] Mullins and associates[38] have issued a report detailing the operating instructions, procedures, and equipment recommended for use in the Los Alamos electrorefining plant now under construction.

Phase equilibria in the plutonium–plutonium trichloride system have been investigated by Johnson and Leary[39] at temperatures up to 1180°C. The salt-rich eutectic exists at 7 mole % plutonium and 740°C, which is also the monotectic temperature. The metal-rich eutectic point is at a composition greater than 99 mole % plutonium and could not be determined accurately. No evidence for a plutonium halide other than $PuCl_3$ was observed.

Owing to the success achieved at Argonne National Laboratory in the reduction of uranium oxides by zinc-magnesium alloys in the presence of molten fluxes,[40] several tests were performed to evaluate the direct reduction of plutonium dioxide to metal in similar systems.[41] A series of plutonium dioxide reduction experiments was carried out to evaluate the effect of flux composition on the conversion to plutonium metal. The quantity of plutonium dioxide employed in the tests was sufficient to produce a 1 wt.% plutonium concentration in the zinc–5 wt.% magnesium alloy on complete reduction. The results of the tests are presented in Table V-3. The reduction of PuO_2 to metal was rapid and complete in all fluxes used, and the degree of reduction appeared to be relatively independent of the flux composition. The fact that reduction of PuO_2 does not require magnesium chloride as a major flux constituent, as is required for UO_2 and ThO_2 reductions,[40,42] may represent a method for separating plutonium from uranium and thorium.

Table V-3 EFFECT OF FLUX COMPOSITION ON REDUCTION OF PLUTONIUM DIOXIDE[41]

[Experimental Conditions: Temperature, 800°C; Mixing Rate, 800 rpm; Crucible, Tantalum; Atmosphere, Argon; Metal, 600 g of Zinc–5 Wt.% Magnesium; Flux, 300 g (of Specified Composition); PuO_2, 7.13 g (1.0 Wt.% Plutonium in Metal Phase at 100% Reduction)]

Flux composition	Plutonium concentration after 120 min, wt.%		PuO_2 reduction,* %
	In metal	In flux	
95 mole % $MgCl_2$–5.0 mole % MgF_2	0.95	0.0109	99.5
47.5 mole % LiCl–47.5 mole % $CaCl_2$–5.0 mole % MgF_2	0.88	0.0007	99.94
47.5 mole % KCl–47.5 mole % $CaCl_2$–5.0 mole % MgF_2	0.97	0.0034	99.9
47.5 mole % KCl–47.5 mole % LiCl–5.0 mole % MgF_2	0.95	0.0038	99.4

*Based on amount of plutonium remaining in the flux after 120 min.

The extent of plutonium dioxide reduction appears to be determined by the distribution coefficient of plutonium between the metal and the flux. The distribution coefficients

$$K_d = \frac{\text{plutonium concentration in flux, wt.\%}}{\text{plutonium concentration in metal, wt.\%}}$$

for plutonium between magnesium chloride and zinc-magnesium alloy show a minimum at 10 wt.% magnesium in the alloy. A similar minimum at 10 wt.% magnesium was found in tests involving the reduction of plutonium dioxide with a flux composition of 47.5 mole % $MgCl_2$, 47.5 mole % $CaCl_2$, and 5 mole % MgF_2 (Fig. V-2). (J. Barghusen)

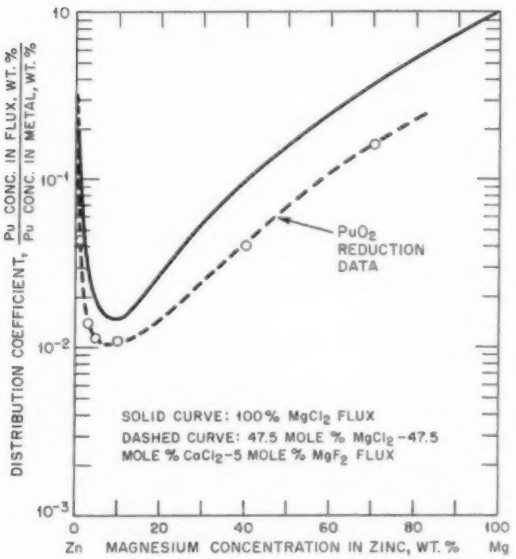

Fig. V-2 Distribution of plutonium between zinc-magnesium alloy and magnesium chloride.[41] Conditions: temperature, 800°C; mixing rate, 300 rpm (solid curve) and 800 rpm (dashed curve); atmosphere, argon; crucible, tantalum.

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